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THE INFLUENCE OF SURFACE STRUCTURE ON THE CATALYTIC ACTIVITY OF ALUMINA SUPPORTED TRANSITION METAL OXIDES: A STUDY OF CARBON MONOXIDE AND METHANE OXIDATION presented by

Paul Worn Park

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THE INFLUENCE OF SURFACE STRUCTURE ON THE CATALYTIC ACTIVITY OF ALUMINA SUPPORTED TRANSITION METAL OXIDES: A STUDY OF CARBON MONOXIDE AND METHANE OXIDATION

By

PAUL WORN PARK

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ABSTRACT

THE INFLUENCE OF SURFACE STRUCTURE ON THE CATALYTIC ACTIVITY OF ALUMINA SUPPORTED TRANSITION METAL OXIDES: A STUDY OF CARBON MONOXIDE AND METHANE OXIDATION

By

PAUL WORN PARK

The projects described in this thesis examine the effect of rare earth and transition metal oxide promoters on the structure and reactivity of base metal oxide/alumina catalysts for total oxidation reactions. The research involves the preparation and testing of alumina supported single and mixed metal oxide catalysts designed for total oxidation reactions. The catalysts were prepared with various active phase loadings, promoter contents, and precursors to control the chemical state and structure of supported phases. The identification and quantification of various supported phases have been determined using surface (XPS), bulk (XRD, ESR, FTIR, TGA, BET), and microprobe (TEM) techniques. The information derived from these techniques was correlated with CO and CH₄ oxidation activities to identify active sites and to examine the effect of promoter on the structure and reactivity of the catalysts.

The effect of crystallinity on the photoreduction of Ce(IV) species during XPS analysis of CeO₂ samples and Ce/Al₂O₃ catalysts has been determined. The crystallinity of the samples was controlled by varying the calcination temperature or by using different Ce precursors (ammonium Ce(IV) nitrate and Ce(IV) methoxyethoxide). XPS, XRD, and TEM results indicated that the amorphous cerium oxide was reduced more extensively than the crystalline material during XPS analysis.

XRD, XPS, and ESR results indicated that an isolated copper surface phase, an interacting copper surface phase, and large CuO crystallites are formed on Cu/Al₂O₃ catalysts, depending on Cu content. The crystalline CuO and isolated copper surface phase has been assigned to the active site for CO and CH₄ oxidation, respectively. Cu/Al₂O₃ catalyst prepared using Cu(II) ethoxide showed higher Cu dispersion, less crystalline CuO, and lower oxidation activity for CO and CH₄ than the catalyst derived from Cu(II) nitrate. For Cu/Ce/Al₂O₃ catalysts, Ce had little effect on the dispersion and crystallinity of the copper species. However, Cu addition decreased the Ce dispersion and increased the amount of crystalline CeO₂. Cerium addition dramatically increased the CO oxidation activity, but it had little effect on CH₄ oxidation. This indicated that cerium strongly interacted with crystalline CuO, but not with copper surface phase.

The characterization of Cr/Al₂O₃ catalysts indicated that Cr was present as a highly dispersed Cr⁶⁺ surface phase, Cr³⁺ clusters, and large Cr₂O₃ crystallites, depending on Cr content. The active phase for CH₄ oxidation has been assigned to a Cr(III)-Cr(VI) interaction species. For the Cu/Cr/Al₂O₃ catalysts, Cu addition decreased the dispersion of the chromium phase by reacting selectively with a dispersed Cr³⁺ species to form CuCr₂O₄. The Cu dispersion also decreased with increasing Cr loading due to the formation of CuO and CuCr₂O₄. These phases contributed to the catalytic activity of CO oxidation with increasing Cr content up to Cr/Al = 0.054. For further Cr addition, the catalytic activity decreased due to the decrease in catalyst dispersion or to encapsulation of the active site by excess Cr species.

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Chapter 1

Air Pollution and Pollution Control Catalysts

1.1. Air Pollution

1.1.1. Introduction

In recent years, there has been great concern about environmental problems which have resulted from the development of technologies. A tremendous amount of governmental and scientific effort has been exerted to improve the environment all over the world. While we still want to continue our economic growth which creates more products, more jobs, and a more comfortable and pleasurable lifestyle, at the same time, we also want to protect ourselves from an environmental crisis. One of the answers to this apparent paradox (economic growth and a clean environment) can be addressed by developments in catalytic science and technology [1].

The definition of air pollution was given by Seinfeld [2] as follows, 'any atmospheric condition in which substances are present at concentrations above their normal ambient levels to produce a measurable effect (i.e., undesirable effect) on human beings, animals, plants, or materials'. By this definition, the substances can be any natural or artificial airborne chemicals which may exist in the atmosphere in gas, liquid, or solid forms. Since it is impossible and unreasonable to eliminate all man-made emissions, it is more desirable to focus on the reduction of pollutants to the level of no harmful effects. The air pollution problems cannot be solved by the efforts of a few scientists. The study of emission sources, behavior of emissions in the atmosphere, and the effect of emissions on animals and plants requires a knowledge of the chemistry of combustion, engineering aspects of the equipment design, meteorology, mechanics, atmospheric chemistry, aerosol physics, physiology, medicine, plant pathology and so on. Since air pollution is also a global problem which requires international cooperation, not only science and technology fields but also social, economic, and political factors may play a major role in the abatement of air pollution problems.

1.1.2. Origin and Effect of Air Pollutants

The origin of air pollution is an emission source. Major emission sources are transportation, electric power generation, refuse burning, industrial and domestic fuel burning, and industrial process. These emission sources produce air pollutants such as carbon monoxide, carbon dioxide, sulfur compounds, nitrogen compounds, alcohol, aldehyde, hydrocarbons, halogen compounds, particulate matter and radioactive compounds. These air pollutants cause many undesirable effects such as respiratory illness, visibility diminution, damage to animals and plants, and possibly catastrophic effects on the global scale [2-4].

2

Carbon Monoxide and Dioxide(CO and CO₂): With the exception of CO₂, CO is the most abundant air pollutant in the lower atmosphere especially in urban areas. The major source of CO is the incomplete combustion of fossil fuels from automobile exhaust. Carbon monoxide is quite stable in the air and the rate of conversion to CO₂ is very low. Carbon monoxide is a poisonous inhalant because it has a strong affinity (250 times greater than oxygen) for hemoglobin and replaces oxygen. CO₂ is not normally regarded as an air pollutant according to the definition of air pollution and is an inevitable final product of the combustion process. However, although CO₂ effects may have been small to date, it may cause a significant effect in the future when its concentration increases in the atmosphere. CO₂ absorbs infrared terrestrial radiation and can increase surface and atmospheric temperatures (green-house effect).

Sulfur Oxides (SO_x) : The sources of atmospheric sulfur oxides (SO_2, SO_3) are combustion of fossil fuels (typically coal), decomposition and combustion of organic matter from electric power generation and industrial sources. SO_x also appears in auto exhaust gases depending on the sulfur content of the fuel. SO_2 is highly soluble and absorbed in the upper respiratory system causing constriction of the airways. It also contributes to acid rain.

Nitrogen oxides (NO₃): The primary sources of nitrogen oxides (predominantly NO and less than 5% NO₂) are high temperature combustion processes (particularly above 1500 °C) and the oxidation of fuel containing nitrogen compounds. The combustion process fixes atmospheric nitrogen to produce first nitrogen monoxide (NO), which will be converted into nitrogen dioxide (NO₂). Under the action of solar radiation NO₂

dissociates into NO and atomic oxygen which gives rise to the formation of ozone O_3 . The ozone produces a narrowing of the airways in the lung and accelerates an aging of lung tissue by oxidation. Organic molecules react with ozone to form free radicals which in turn act as a catalyst for the oxidation of NO and hydrocarbons. Nitrogen oxides are known to cause bronchitis, pneumonia, susceptibility to viral infection and damage to the immune system. They also contributes to acid rain, urban smog, and ozone.

Hydrocarbons: The combustion of gasoline is a major source of hydrocarbon emissions as a result of either simple evaporation before combustion or incomplete combustion. Benzene, its analogs, and aromatic polycyclic hydrocarbons are responsible for mutagenic or carcinogenic action. Hydrocarbons along with nitrogen oxides are a very important contributors to photochemical smog.

Particles: Fine particles (mostly fly ash), which consist of inorganic and organic compounds of high molecular weight, are emitted from combustion systems (especially coal combustion). The particles, due to their small diameter, penetrate deep into the lungs and are retained for indefinite periods of time. Motor vehicles emit a number of metals such as Pb, Cr, Mn, Ba, V, Fe, Al, Cd, and Ni from engine exhaust, panel body alterations, tires, brakes systems, etc. Many of these metals are toxic, in particular Cd, Ni, Cr are carcinogenic, while Mn affects to the nervous system.

1.1.3. Pollution Control Techniques

Control techniques for limiting pollutant formation and emission at the source can be classified into three groups: modification of the basic process, substitution of cleaner-

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burning fuels, and cleaning of the effluent gases before release to the atmosphere. The particular technique is selected depending on pollutants involved, the process responsible for pollutant formation, and the required degree of control [2]. Cleaning of effluent gases has received the most attention and is the most widely used among the three control techniques.

The most frequently used technique to clean effluent gases from emission sources is the application of add-on devices. These devices are usually divided into two types: recovery and incineration devices. The suitable control device is selected on the basis of stream-specific characteristics and desired control efficiency.

1.1.3.1. Recovery techniques

One of the recovery techniques is the gas absorption method which uses a liquid solution capable of dissolving the pollutant gas molecules. Absorption is a diffusion process that involves the transfer of molecules from the gas state into the liquid state because of the contaminant concentration gradient between two phases. For best operation, the contaminants should be readily soluble in the liquid phase and undergo an irreversible reaction with a scrubbing reagent. An alternative recovery technique is to adsorb pollutants on a solid surface which can retain gas molecules by physisorption or chemisorption. Adsorption is a semi-continuous, diffusion-limited, surface area dependent process that involves percolation of a gas through a solid bed. Adsorption depends on selectivity and high capture efficiency which usually requires a significant mass-transfer gradient from the gas phase to the surface [2,5].

1.1.3.2. Combustion Techniques

The combustion method involves chemical alteration of the pollutant to nonpollutant molecules through thermal or catalytic incineration of the waste gases. Thermal incineration is currently the most widely used method to control emissions from industrial volatile organic compound (VOC) sources because it can provide high (> 99%) VOC destruction efficiencies when operated above their auto-ignition temperatures (usually 500 - 1000 °C) [6,7]. In addition, thermal incinerators are relatively simple and economical to install and operate. Thermal incinerators are applied principally when low concentrations of combustible materials are present in a waste stream or when a reliable supply of waste gas is available to use as a fuel for preheat burners. Thermal incinerators are generally used when organic aerosols, significant amounts of non-combustible, high boiling point compounds, inorganic materials, dusts, catalyst poisons or inhibitors are present in the waste gas stream. However, thermal incineration requires a high fuel cost since the waste gases need to be heated up to high operating temperatures for effective operation. The high operating temperature of thermal incinerators may produce undesirable secondary emissions such as NO_x (via fixation of atmospheric nitrogen) and dioxins (via destruction of chlorinated hydrocarbons) and create difficulties in mechanical design [5-7].

1.2. Pollution Control Catalysts

1.2.1. Introduction

1.2.1.1. Principle of Catalytic Incineration

The objective of introducing a catalyst in a combustor is to carry out heterogeneous oxidation on its surface. By choice of a suitable catalyst, one can ensure that an activation energy for a heterogeneous reaction is much lower than that for a purely homogeneous reaction. For instance, the activation energies for the homogeneous oxidation of propane are approximately 25-50 kcal/mol, while those for heterogeneous oxidation reactions are approximately 10-20 kcal/mol. Consequently, appreciable heterogeneous oxidation rates can be achieved for temperatures and fuel concentrations much lower than those required for the homogeneous reactions to proceed [8]. Therefore, catalytic oxidation is an efficient and effective method for burning low heating value gaseous fuels and for the destruction of trace organic contaminants in air [9]. To obtain optimal performance from a combustor, the catalyst system should possess several properties. First, the catalyst should be able to ignite a fuel/air mixture at the lowest possible temperature (low light off temperature). Second, the catalyst activity should be sufficiently high to maintain complete combustion at the lowest temperature and the highest mass throughput. And finally, the support should have a large surface area, low pressure drop, and high thermal and shock resistance [8].

1.2.1.2. Advantages of Catalytic Pollution Control

Primary advantages of using catalysts for emission control are that pollutants can be completely oxidized at relatively low temperatures and consequently the formation of NO_x is greatly suppressed compared to thermal incineration [10]. For the thermal process, high temperature is normally maintained by burning extra fuel which represents up to 40 % of total operating cost. Therefore, operating cost is lower than for thermal incineration. The decreased temperature also allows the use of corrosion resistance alloys for reactors rather than replaceable ceramic linings which corrode rapidly in the thermal incinerator [11]. The introduction of a heterogeneous catalyst also allows better control of oxidation over wider air/fuel ratios. If a fuel concentration is too low to maintain catalyst temperature, a catalyst bed can be heated effectively to the temperature at which oxidation is initiated. In addition, the use of a catalyst improves energy recovery by minimizing energy loss as visible light (i.e. non-flammable combustion) [12]. These advantages have led to widespread application of catalytic incineration for the control of waste gas emitted from industrial processes and automobile converters.

1.2.1.3. Disadvantages of Catalytic Pollution Control

The primary disadvantage of using catalysts for emission control is that all catalysts are eventually deactivated physically and chemically. Physical deactivation results from mechanical attrition and sintering which lead to loss in active components and surface area, respectively. Chemical deactivation results from presence of impurities which can lead to poisoning and accumulation of deposits which can lead to fouling. Thus, many catalysts require frequent and costly replacement of a catalyst bed and interruption of process operation [5,13]. Further disadvantages of catalytic combustors are that the volumetric heat release rates and mass transfer coefficients are very low compared to those of the thermal combuster [14]. In addition, destruction efficiency for a given compound may vary depending on the composition of a mixture in an emission stream [15].

1.2.2. Noble Metal Catalysts

1.2.2.1. Advantages of Noble Metal Catalysts

Most commercial catalysts for total oxidation reactions utilize noble metals such as Pt and Pd. Although, in principle, any noble metal (such as Ag, Au, Ru, Os, Ir) may be used as a total oxidation catalyst, their application is limited due to sintering, volatility loss, and irreversible oxidation resulting from excess oxygen present at high temperature. Limited supply and high cost of these metals also minimize their use [8]. Compared to base metal oxides, noble metals have many advantages such as high intrinsic activity for oxidation reactions, high thermal stability, and sulfur poisoning resistance [16]. In addition, Pt and Pd are readily prepared in a highly dispersed form on a number of support materials. For these reasons, only small amounts (0.1-0.5 wt.%) are typically necessary for the production of good combustion catalysts. The high intrinsic activity of these metals is related to their ability to activate H_2 , O_2 , C-H, and O-H bonds [8]. On noble metals, oxygen adsorption is relatively weak. This implies that the mechanism may

proceed through direct electron transfer between reactant and oxygen on metal surface. The general mechanism of oxidation over noble metals is suggested to involve the dissociative adsorption of oxygen [17].

$$O_2 + [] \rightarrow [O_2] \rightarrow 2[O]$$
 (1.1)

where [] represents a surface active site.

1.2.2.2. Disadvantages of Noble Metal Catalysts

While noble metal catalysts have many advantages, there are several problems in the operation of the catalysts. This is especially true for chlorinated hydrocarbon oxidation because such systems are susceptible to Cl₂ and HCl poisoning, byproducts of the reaction [58,59]. Noble metals are deactivated by sintering at temperatures of between 500 ~ 900 °C [8]. Sintering reduces the active surface area and catalyst activity. It has been found that in oxidizing atmosphere, noble metals can disperse as oxides on Al₂O₃ surface at temperatures below the decomposition temperatures of the oxides (PtO₂, 585 °C; PdO, 790 °C) [18]. PtO₂ interacts weakly with γ -Al₂O₃ surface so that the Pt dispersion decreases and large metallic crystallites form at temperatures greater than 600 °C under oxidizing conditions [16]. The prolonged exposure of Pd to oxygen has been observed to cause structural changes in Pd metal that result in loss of catalytic activity for methane oxidation at temperatures above 450 °C [19]. In addition, catalytic combustors using noble metal catalysts convert very high levels of fuel bound nitrogen to NO_x (50~90

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%) under lean condition [8]. The high price and limited supply are also major disadvantages for using noble metals.

1.2.3. Transition Metal Oxide Catalysts

1.2.3.1. Advantages of Transition Metal Oxide Catalysts

Transition metal oxide catalysts have been considered as suitable substitutes for noble metal catalysts because of their natural abundance and low cost. Current issues are the development of contaminant resistant and thermally stable base metal oxide catalysts for automobile catalytic converters and industrial catalytic incinerators [20]. Transition metal oxide catalysts have greater resistance to certain poisons such as halogens, As, Pb, and P [21] and yield a lower level of fuel bound nitrogen conversion to NO_x (10–20 %), even in lean fuel operation, than noble metal catalysts [8]. Thus, the use of oxide based catalysts such as $Cr_2O_3-Co_3O_4$ [22] and NiO [23] appears to be very promising for NO_x control from both thermal and fuel bound nitrogen. Metal oxide catalysts typically have lower catalytic activity and higher light-off temperatures than noble metal catalysts. However, for typical catalytic combustion, catalysts are operated under a diffusion control region where their activities are comparable to those of the noble metals and under such operation, the catalytic activity (kinetic control) plays a secondary role in determining the reaction rate [8].

1.2.3.2. Principles of Transition Metal Oxide Catalysts

Blazowski et al. [24] indicated that Co_3O_4 , Cr_2O_3 , CuO, NiO, MnO₂ and V₂O₅ are potential catalysts for hydrocarbon oxidation. MnO₂ and CuO are promising candidates for olefin oxidation [25,26] and Co_3O_4 possesses the highest activity of base metal oxides for paraffin or large molecular weight olefin oxidation reactions [27]. On the basis of the activity of catalyst per unit surface area, Co_3O_4 and CuO catalysts showed high CO oxidation activity [92].

The activity of the transition metal oxide catalysts for oxidation reactions may depend on redox behavior of metal ions [28], metal-oxygen bond strength [29], and types of oxygen involved in the reaction [30]. In addition, there should be an optimum level of interaction between active sites and reactants. If the interaction is too strong, the catalyst will be deactivated by irreversible chemisorption. If the interaction is too weak, only a small fraction of the surface is covered and the catalytic activity is very low [31]. Low temperature ESR studies have shown that the interaction of oxygen gas with an oxide surface proceeds the following steps [32].

$$O_2$$
 (gas) + $e^- \rightarrow O_2^-$ (adsorbed) (1.2)

$$O_2^{-} + e^{-} \rightarrow 20^{-} (adsorbed)$$
 (1.3)

$$O^{-} + e^{-} \rightarrow O^{2}$$
 (lattice) (1.4)

The mobility of oxygen species is also important for oxidation catalysts because highly mobile oxygen should result in a highly active and non-selective catalyst [9]. Both adsorbed and lattice oxygen participate in a catalytic oxidation process. Haber [33] postulated that surface adsorbed oxygen may generally lead to complete oxidation, whereas lattice oxygen is used for partially oxidized products. This may be because surface adsorbed oxygen is more mobile than lattice oxygen. Though, in principle, either O_2^- or O^- may promote total oxidation, O^- may be more reactive than O_2^- due to its higher mobility. In addition, O^- is known to oxidize CO and H₂ even at -196 °C [30]. Lattice oxygen becomes important when the oxidation processes are at high temperatures (> 500 °C).

Mixtures of these oxides often exhibit greater stability and combustion activity than the single oxides [34-37]. Considerable improvement in thermal stability can be achieved by utilization of complex oxides such as rare earth perovskites [38] and mixed transition metal oxides [39]. Indeed, a binary transition metal oxide catalyst comprised of $Cr_2O_3-Co_3O_4$ supported on alumina has been successfully used for the catalytic combustion of lean propane-air mixtures [40]. Catalysts comprised of $La_2O_3-Cr_2O_3$ also appear to be very promising for oxidation at high temperature [41]. CuO-MnO₂ (hopcalite) [42] and CuO-Cr₂O₃ [43] catalysts are well known as some of the most active oxidation catalysts among base metal oxide catalysts. These catalysts were also studied for the removal of air pollutants such as CO and NO from exhaust gas [44,45]. The synergistic effect of mixed oxide catalysts compared to their individual oxide components may be due to the readily available multiple energy levels of the metals and their associated oxygen anions, which makes the organic reactant more accessible to the active oxygen anions. This also may result in higher surface mobility of oxygen and/or the activated complex as well as electron transport through the lattice [31].

1.2.4. Industrial Waste Treatment Catalysts

1.2.4.1. Volatile Organic Compounds (VOC) Emission

The control of organic emissions from industrial processes was first accomplished by catalytic incineration in the late 1940's [46]. However, after thermal incineration was developed during 1960's [13], the first catalytic system was installed for commercial use in 1975. Catalytic oxidation is widely used for trace contaminant removal in Europe due to the high cost of energy and relatively strict environmental regulations. The Clean Air Act 1990 in the US raised the number of toxic chemicals to be controlled by the year 2000 from 7 to 189 (70 % of these are VOCs) [47]. Both catalytic and thermal combustion are used for controlling VOCs. Some areas where catalysts are used beyond thermal combustion are in can, paper, coating, organic chemical and plywood manufacture, tire production, asphalt blowing, odor control, waste water plants, automotive exhaust, and to remove air contaminants in submarines [48]. For these processes, a highly active and nonselective catalyst is required. Pt shows high oxidation activity for saturated hydrocarbons and high molecular weight species [49]. Pd is preferred for CO, olefins, methane and low molecular weight olefin oxidation [50]. Base metal oxide catalysts are used less frequently for waste gas which is relatively free of contaminants or for fluidized bed processes in which the catalytic surface is refreshed by abrasion [51]. The preferred support for organic abatement catalysts is either ceramic (cordierite) or metallic (aluminum, stainless steel) monolith or honeycomb. These support materials can minimize pressure drop with parallel channels (200-400 channels per square inch). Most commonly 0.1-0.5 wt.% Pt on high surface area γ -Al₂O₃ is used for a bead or washcoat on a monolith. In limited cases, a small amount of Pd or Rh is added to promote a particular reaction where the Pt may be deficient. If the feed contains a large amount of sulfur (> 50 ppm S), less reactive carriers such as TiO₂ or α -Al₂O₃ are used for Pt [10] to avoid formation of sulfates.

An air stripper is used to remove VOCs from contaminated ground water. The emission from air strippers contains a wide range of compounds and concentrations of VOCs including chlorinated organics. Chlorinated organics cause byproduct formation in thermal oxidation systems. For instance, thermal destruction of polychlorinated biphenyls (PCBs) requires temperatures of at least 1200 °C and residence times of over 1 second. Standard municipal incinerators merely vaporize and release PCBs into the atmosphere [52] or produce even more toxic polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) [53-55]. Hence, there is a compelling need for development of economically viable, lower temperature processes capable of effectively treating incinerator flue gas or other effluents that may be contaminated with PCB vapors [56].

Catalytic combustion systems may be the answer for air stripper emission control due to its low temperature operation, relatively humidity insensitive, and its compatibility with low gas concentrations [57]. Transition metal catalysts are suitable candidates for VOC control because noble metals (Pt, Pd) are susceptible to Cl₂ and HCl poisoning from the destruction of chlorinated hydrocarbons [58-62]. Cr₂O₃/Al₂O₃ is considered to be a suitable catalyst for chlorinated hydrocarbon oxidation because it produces low levels of Cl_2 which is a more toxic compound than HCl. Weldon and Senkan [63] have determined the Cl_2 selectivity for CH_3Cl oxidation to be in the 3-7 % range over Cr_2O_3/Al_2O_3 , whereas a 19-42 % range of Cl_2 selectivity was reported for copper based catalysts [64].

1.2.4.2. NO_x Emission

 NO_x consists primarily of NO and NO_2 , which are produced in all combustion processes by the oxidation of N_2 and fuel bound nitrogen. At temperatures higher than 1500 °C, the reaction proceeds at appreciable rates through the Zeldovich mechanism [65].

$$N_2 + O \rightarrow NO + N \tag{1.5}$$

$$N + O_2 \rightarrow NO + O \tag{1.6}$$

$$N + OH \rightarrow NO + H \tag{1.7}$$

The rate of the above reactions is controlled by reaction (1.5), which has a high activation energy and, as a result, thermal NO_x formation is highly temperature dependent. If a compound in the combustion process has bound nitrogen (e.g., pyridine), NO_x is readily formed at much lower temperature through an oxidation process [66]. Recently, the emissions of N₂O from fiber production plants has received attention due to its potential to contribution to global warming (strong infrared absorptivity). The major contribution to NO_x generation is stationary sources. NO_x emission from power plants and lean burn engines cannot be controlled by three-way catalysts due to the uncontrolled stoichiometric air/fuel ratio. The most effective NO_x control strategies are catalytic decomposition of nitrogen oxides and selective catalytic reduction [67].

Catalytic NO_x decomposition: The decomposition of NO_x to nitrogen and oxygen is one of the most challenging approaches to remove NO_x from exhaust gases. Thermodynamically, NO should be decomposed to its constituents elements at low temperature.

NO (g)
$$\rightarrow 1/2N_2 + 1/2O_2 \quad \Delta G^\circ = -20.7 \text{ kcal/mol}$$
 (1.8)

Accordingly, a catalytic NO_x decomposition method could be the simplest and cheapest technique since no added reductant is necessary. Silver promoted Co_3O_4 [68], perovskite type oxides [69,70], Pt/Al₂O₃ [71], Rh/Al₂O₃ [72], Cu-ZSM-5 [73] have been reported to be active catalysts for NO_x decomposition. Cu-ZSM-5 catalyst is considered to be the most active system [67]. However, at present these catalysts are not active enough under commercial conditions [74]. Furthermore, the Cu-ZSM-5 catalyst is poisoned by SO₂ [75] and by oxygen in the feed gas or produced from NO decomposition [76].

Catalytic reduction of NO_x by ammonia: Selective catalytic reduction (SCR) of NO_x using NH_3 was first discovered with Pt catalysts in excess amounts of oxygen [77]. The technology of selective catalytic reduction with ammonia was well developed in Japan and

Western Europe to control of NO_x emissions from electricity generating power plants. The Clean Air Act 1990 will prompt widespread use of SCR technologies in USA.

The desired reactions are:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$
 (1.9)

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$
(1.10)

The undesired reactions are:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$
 (1.11)

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
 (1.12)

Pt catalysts were not applicable because they have poor selectivity for NO_x reduction at temperatures above 250 °C. Above 250 °C, a V₂O₅/Al₂O₃ catalyst was used first, but was restricted to sulfur free exhaust gases due to its high sensitivity to poisoning. SO₂ is converted to SO₃ which reacts to form sulfates (Al₂(SO₄)₃) which plug catalyst pores and cause deactivation. Further, as the catalyst deteriorates, the activity at a fixed NH₃/NO_x ratio decreases and slippage of NH₃ increases, with resultant discharge of NH₃ into the atmosphere [67]. Therefore, an alternative method of NO_x control has been developed using vanadia/titania catalysts. These catalysts facilitate reaction between NO_x and NH₃ or hydrocarbons in the presence of oxygen. SiO₂, WO₃, MO₃ can be used as promoters. A key to the success of the V/Ti catalyst is that it is not poisoned by SO₂

because the TiO₂ carrier is non-sulfating under operating conditions [78-80]. V₂O₅ based catalysts operate best in the temperature range between 260-450 °C. The maximum exposure temperature for this catalyst must not exceed 450 °C, because the active anatase phase of TiO₂, with a surface area of 80-120 m²/g, irreversibly converts to rutile, with a surface area of less than 10 m²/g. Recently, Cu/Zeolite catalysts have been developed that function at higher temperatures over a broader range of temperatures than Pt and V₂O₅ based catalysts [81]. These catalysts have much lower tendency to oxidize ammonia to NO_x and the maximum operating temperature is about 600 °C. Above 600 °C, the zeolite is deactivated by a de-alumination process whereby the Al ions migrate out of the SiO₂-Al₂O₃ structure [10].

The SCR technique using ammonia has received much attention because ammonia is a very selective reducing agent to NO_x under oxidative conditions. The other reactants such as CO, H₂, CH₄ and hydrocarbons react readily with oxygen in the gas stream. There are several disadvantages of using ammonia as a reductant. NH₃ is more expensive than hydrocarbons especially methane, it requires special handling and storage, and a sophisticated metering system is needed to avoid NH₃ leakage [10].

Catalytic reduction of NO_x by hydrocarbons: Reduction of NO_x by natural gas or other hydrocarbon has recently attracted much attention as a possible new de-nitrification process for exhaust gases from power plants, diesel and lean-burn gasoline engines. The motivation to develop NO_x reduction in lean environments using hydrocarbons is to improve fuel economy. Operating an internal combustion engine under lean conditions
improves the combustion efficiency, power output, and decreases the emission of the greenhouse gas CO_2 . Additionally, in many new power plants, natural gas is commonly used as a fuel and is readily available [10,67,82].

$$CH_4 + 2NO + O_2 \rightarrow N_2 + 2H_2O + CO_2$$
 (1.13)

Catalysts comprised of copper ion exchanged zeolite (Cu-ZSM-5) were the first discovered to be active and selective for NO_x reduction with propane at 500 °C under oxidative conditions. Cu-ZSM-5 catalyzed NO₂ reduction by C₂H₄, C₃H₆, C₄H₈, C₃H₈ in the presence of O_2 [83,84] H-ZSM-5 was a particularly good catalyst for the reduction of nitric oxide by C_3H_8 in the presence of O_2 [85]. Its activity is actually promoted by the presence of O_2 , but it is ineffective at lower temperatures and inhibited by H_2O_1 . In contrast, the use of ethylene or propene reduces NO_x at lower temperatures (160 -200 °C). An Fe ion exchanged mordenite catalyst was recently reported to be most active for NO_2 reduction by C_2H_4 in the presence of O_2 at 200 °C [86]. Since CH₄ is a major hydrocarbon emission from a gas-cogeneration system, such as a electric power plant, it would be advantageous to develop a catalyst which is active for reduction of NO_x by CH₄ in lean conditions [87,88]. Li and Armor [89] have found that a Co-ZSM-5 catalyst showed potential for using natural gas as a reductant. However, the reaction rate was slow and was inhibited strongly by H_2O . Noble metal catalysts are also regarded as promising. Alumina supported Pt catalysts show higher activity and durability than Cu-ZSM-5

catalysts under real diesel exhaust conditions [90]. However, at present, no commercial process has been developed for catalytic reduction of NO_x under oxidative conditions.

1.2.5. Automobile Emission Control Catalysts

The development of catalytic reactors for cleaning exhaust gases of automobiles has been stimulated successfully by legislation motivated by environmental and political issues. In 1959 and 1960, laws on motor vehicle emission standards were first enacted and these standards could be met with the modification of engine parameters. The Clean Air Act of 1970 announced further tightening of the standards that went well beyond existing technology and catalytic research increased considerably. The catalytic converter has been considered as the only technology available for meeting the stringent automobile exhaust standards [91].

Automobile catalytic converters have been used in the US since 1974 (1975 model year vehicles) in order to meet emission standards. The initial objective was to reduce the emission of CO and hydrocarbons. The engine was operated in the fuel rich side and the concentrations of CO and hydrocarbons are relatively high, whereas the NO_x concentration is low. The nitrogen oxide standard could be met by using exhaust gas recirculation which leads to the formation of lower levels of nitrogen oxides by reducing the combustion flame temperature in the engine [91]. The oxidation catalysts used until 1979 were a combination of Pt and Pd and operated in the temperature range of 250 - 600 °C with space velocities from 10,000 - 100,000 l/hr depending on the engine size and driving mode. Typical catalyst compositions were Pt and Pd in a 2.5:1 or 5:1 ratio,

ranging from 1.6-3.1 g/car [10]. Many base metal oxide candidates were also investigated in this period, such as Cu, Cr, Ni, Mn [92,93].

Since 1979, the NO_x standards tightened and exhaust gas recirculation alone was no longer sufficient to control nitrogen oxides emission. In the beginning, the dual bed system with separate reduction and oxidation catalysts was considered due to difficulties in controlling stoichiometric air/fuel ratio. The engine was operated under fuel rich conditions for the first bed so that a catalyst could reduce NO_x with H₂, CO and hydrocarbons. Remaining exhaust gases would be oxidized in the second bed with air injection [94]. The activity of alumina supported noble metal catalysts for NO reduction by CO-H₂ mixture was reported in the order Ru>Rh>Pd>Pt [95]. However, Ru, Pd, and Pt were not proper catalysts for NO_x reduction beds. Ru was found to be volatile by forming RuO₃ or RuO₄ when the engine exhaust was oxidizing and the temperature exceeded about 700 °C [96]. In addition, RuO₄ is a highly toxic compound. Pt and Pd catalysts are less useful as NO reduction catalysts due to large production of NH₃ which would be reoxidized to NO_x in second oxidation bed. Rh was suitable for the NO_x reduction bed because it has a high activity for NO_x reduction [95], is less inhibited by CO and sulfur [97], and forms less NH_3 than Pt or Pd. It also has an extended NO_x conversion window [98].

The next generation of catalysts named three-way catalyst (TWC) could catalyze all reactions simultaneously: hydrocarbons and carbon monoxide are oxidized to CO_2 and H₂O, while nitric oxides are reduced to N₂. The noble metal Rh combined with Pt is able to do both sets of reactions if the engine exhaust is operated close to stoichiometric air/fuel ratio. A typical example of the influence of air/fuel ratio to the conversions is

given in Figure 1.1. On the rich side (air<fuel), the NO_x reduction occurs readily, while the CO and hydrocarbon oxidation reactions are prevented by insufficient O2. As the air/fuel ratio approaches the stoichiometric point (air-fuel), simultaneous catalytic conversion of all three occurs in a narrow window. On the lean side (air>fuel), the CO and hydrocarbon conversions are high, but at the sacrifice of the NO_x reduction. A special control system to maintain the stoichiometric air/fuel ratio at all times required an advance in this technology. This was made possible by the development of the O₂ sensor, which was positioned before the catalyst bed in the exhaust manifold [99]. The catalysts in use contain Pt, Pd, and Rh as major constituents supported on La₂O₃ (and/or BaO) stabilized (1-2 wt.%) alumina. The alumina is usually introduced as a washcoat (about 15 wt.% and 30-50 µm thick) to a ceramic honeycomb monolith made of cordierite (2MgO·2Al₂O₃·5SiO₂) [100] containing 200-400 square channels per square inch. A converter typically contains 1-3 g Pt and 0.1-0.5 g Rh and 0-3 g Pd. Pt is an effective oxidation catalyst for CO and the complete oxidation of hydrocarbons. Pd is more active than Pt to promote the oxidation of CO and hydrocarbons but is more sensitive to poisoning and sintering than Pt in the exhaust environment. Both Pt and Pd promote the reduction of nitric oxide, but they are less effective than Rh. Rh also contributes to CO oxidation, but is mostly required for NO_x reduction. In addition to the noble metals, three way catalysts contain CeO₂ and possibly other additives such as La, Ni, Fe. These base metal additives are believed to improve catalyst performance by extending conversion



Figure 1.1. Simultaneous conversion of hydrocarbon (HC), CO, and NO_x for TWC as a function of air/fuel ratio. (From Heck, R. M.; Farrauto, R. J. Catalytic Air Pollution Control: Commercial Technology; Van Nostrand Reinhold: New York, 1995).

during the rapid air/fuel ratio perturbations and help to stabilize the alumina support against thermal degradation [91].

Ceria may be added at a loading of 10-30 wt.% to the washcoat of three-way catalysts to store oxygen, promote the water-gas shift reaction, stabilize the noble metals against thermal damage, and to alter CO oxidation kinetics [101,102]. CeO₂ enhances NO_x conversion to N_2 by its ability of oxygen storage derived from NO_x decomposition during lean condition. Stored oxygen is then available for reaction with CO and hydrocarbons during subsequent rich condition [103]. This oxygen storage behavior broadens the operating air/fuel ratio window of the catalyst [104]. Ceria has been shown to enhance the decomposition of NO by extending the time before the noble metal catalyst is deactivated by the accumulation of surface oxygen derived from NO decomposition. For instance, Rh/CeO₂ is deactivated more slowly than is Rh/Al₂O₃ during NO decomposition, probably due to oxygen spillover from the noble metals to the reduced ceria [105]. In addition, ceria addition to an alumina supported Rh catalysts was shown to enhance NO reduction activity at low temperatures by decreasing the apparent activation energy for the reaction of CO with NO and by shifting to positive order the dependence of the rate on NO partial pressure [106].

The reactions are indicated below:

Rich condition:
$$2\text{CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2$$
 (1.14)
 $2\text{CeO}_2 + \text{C}_x\text{H}_y \rightarrow \text{Ce}_2\text{O}_3 + \text{mCO}_2 + \text{nH}_2\text{O}$ (1.15)

Lean condition:
$$Ce_2O_3 + \frac{1}{2}O_2 \text{ (or NO)} \rightarrow 2CeO_2$$
 (1.16)

Another benefit of CeO_2 is that it is a good steam-reforming (or water gas shift) catalyst and catalyzes the reaction of CO and hydrocarbons with H₂O to produce H₂ in the rich condition. Then the H₂ reduces a portion of the NO_x to N₂:

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{1.17}$$

$$C_xH_y + zH_2O \rightarrow nH_2 + mCO_2 \qquad (1.18)$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$
 (1.19)

Ce is the component mainly responsible for the release of H_2S gas by reducing Ce(SO₄)₂ which is formed with SO₃ and CeO₂ in the lean mode. Nickel has been found to be an effective scavenger of H_2S [107]. Lanthanum is added to the alumina washcoat for thermal stabilization [108, 109].

Recently, the replacement of Pt and/or Rh with Pd has been studied for TWC because Pd is relatively less expensive than Pt and Rh [110]. First, the Pd/Rh catalyst was developed for an automotive application [111,112] and then the Pt/Pd catalyst was developed to further reduce TWC cost [111].

Although three way catalysts have been developed which successfully control automobile emissions, they still need to be improved. A major challenge in this field is to develop a catalytic technology which removes NO_x under lean-burn conditions with the

objective of increasing fuel efficiency and environmental protection with a lower level of

CO₂ production [67].

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Chapter 2

Catalysts Preparation and Characterization Techniques

2.1. Preparation of Catalysts

Heterogeneous catalysts used in our work consist of two or three components: the active component, promoter, and support. The active component is responsible for a catalytic reaction. The promoter is catalytically inactive for a reaction, however, it enhances the catalytic performance through interaction with the active component. For Cu/Cr/Al₂O₃ and Cu/Ce/Al₂O₃ catalysts of interest in our study, Cu is the main active component for CO and CH₄ oxidation and Cr and Ce are considered as promoters. The support plays a role of carrier for the active phase or promoter. The support provides a large surface area and disperses an active phase on it in order to maximize the surface area of the active phase. The γ -alumina used in our study provides about 200 m²/g surface area and 0.6 mL/g pore volume. Alumina is quite inactive for CO and CH₄ oxidation in our study. In other cases, alumina can be used as a catalyst by itself for alcohol dehydration, alkene isomerization, and deuterium exchange reaction [1].

2.1.1. γ-Al₂O₃

2.1.1.1. Preparation of γ -Al₂O₃

Aluminas exist as a various amorphous and micro-crystalline forms which can be distinguished by X-ray diffraction. γ -Al₂O₃ is the most important catalyst support due to its thermally stability, controllable surface acidity, and high surface area [2]. Aluminum metal can be dissolved in both acidic and basic solvents because of its amphoteric character. Dissolved aluminum species will exist as solvated Al³⁺ ions in acidic solutions (< pH 2) and aluminate ions (AlO₄⁵⁻) in basic solutions (> pH 12). From using an aqueous acidic Al³⁺ solution (e.g. aluminum sulfate solution), aqueous basic AlO₄⁵⁻ solution (e.g. sodium aluminate solution), or mixture of the basic and the acidic solution, precipitation (aluminum hydroxide) can be obtained if the pH of the solution is properly controlled by addition of extra acid or base. The various structures of aluminas are generally prepared by subsequent dehydration (aging or heating) of the precipitated aluminum hydroxide. Since the structure transformation is determined by kinetic factors rather than thermodynamics, a mixture of different alumina phases are frequently obtained [3]. The transformation of aluminas observed upon aging and heating is shown in Figure 2.1.

2.1.1.2. Structure of γ -Al₂O₃

The oxygen arrangement in γ -Al₂O₃ is cubic close packing, with occupation of the cations (Al³⁺) located partially in tetrahedral and octahedral sites. This arrangement is similar to the spinel structure (e.g. MgAl₂O₄) which contains Mg²⁺ ions in tetrahedral and Al³⁺ in octahedral interstices. The unit cell of a cubic close packed structure





is shown in Figure 2.2. A face centered cube (fcc) contains four oxygen atoms, four octahedral and eight tetrahedral sites. The atomic ratio of metal to oxygen of a true spinel structure is 3:4, as in Mn_3O_4 , Fe_3O_4 or Co_3O_4 , while the atomic ratio of alumina is 2:3. Therefore, there are more cation vacant sites in the Al_2O_3 structure (so called defect spinel) than in a true spinel [2]. The unit cell consists of 32 oxygen and 21-1/3 aluminum atoms, therefore 2-2/3 cation vacant sites per unit cell occur in the lattice [1]. These vacant sites sometimes cause formation of solid solutions with metal cations during catalyst preparation or aging at high temperature. The formula of the γ -alumina is given formally as $H_{0.5}Al_{0.5}[Al_2]O_4$ in which two out of four octahedral sites and one out of the eight tetrahedral sites are occupied by hydrogen and aluminum. However, hydrogen atoms are not located in tetrahedral or octahedral positions. Instead, they are at the surface as OH groups. One OH group is present for every two fcc units [3].

2.1.1.3. Advantages of γ -Al₂O₃ support

Alumina support has been used the most widely in industry among variety of support materials due to its several advantages for practical use [2,4]. Alumina is cheap since its raw materials (Gibbsite or aluminum) are available in large amounts at low cost. Alumina is inert for many chemical reactions, has good mechanical strength (such as attrition resistance, hardness, compressive strength) and maintains high surface area at high temperature. Alumina is amphoteric so that its surface can be electrically charged either positively or negatively according to the pH of solution and can adsorb ions selectively. Active metal (Pt) is dispersed as small clusters on alumina due to the very low



diffusion of the metal. In addition, alumina can be shaped with an accurate control of its porosity.

2.1.2. Catalyst Preparation Techniques

2.1.2.1. Incipient wetness impregnation

Incipient wetness impregnation (or dry impregnation) is widely used in industry due to its simplicity. Accurate control of the amount of support and active ingredient can be achieved by this procedure. The support is contacted with a solution of appropriate active ingredient, corresponding in quantity to the total known pore volume of the support. Capillary force ensures intimate contact of the solution with the interior support surface (meso and micro-pores). The time required for incipient wetness impregnation can be calculated from the following equation, if the contact angle is assumed to be zero

$$t = \frac{4\eta x^2}{\gamma d}$$
(1)

where η is the liquid viscosity, x is the penetration distance into a capillary, γ is the surface tension, and d is the pore diameter. A disadvantage of this method is the limited maximum loading in a single impregnation due to the solubility of the reagent [2]. In our work, all catalysts were prepared by incipient wetness technique with aqueous metal nitrate or alcoholic metal alkoxide solution. The binary component catalysts, such as Cu/Cr/Al₂O₃ or Cu/Ce/Al₂O₃, were prepared by step-wise incipient impregnation methods. The Cr or Ce modified alumina catalysts were prepared first and then Cu was impregnated subsequently on the modified alumina. This step-wise impregnation method allows us to study supported binary oxide catalysts in a simple, systematic way.

2.1.2.2. Ion exchange

Ion exchange is very suitable as a method for preparing atomically dispersed metal [5] or metal oxide [6] catalysts. The principle of this method is based on the fact that the support surface is polarized at the pH of the solution and counter ions are adsorbed by electrostatic attraction. Adsorption phenomena involving ion complexes are determined by the isoelectric point of the support, the pH of the aqueous solution, and the nature of the ion complex. The isoelectric point (or zero point of charge) of γ -alumina is in the range of 7-9 (so called amphoteric point). Therefore its surface charge can be controlled by solution pH in order to adsorb cations or anions selectively. Several disadvantages of the ion exchange method must be considered, such as the adsorption capacity limit of the support, metal complex stability, and the solubility of the support material in acidic or basic solution [7].

2.1.2.3. Grafting

Grafting methods have been developed recently for preparing monolayer catalyst dispersions [8,9]. The method is based on condensation reaction between the metal alkoxide precursor and the hydroxyl group of the support. This chemical reaction yields the corresponding alcohol and a strong metal-support bond. Since alkoxide groups react

with water to be polymerized, nonaqueous solution such as alcohol derivative is commonly used. Several disadvantages of grafting methods are such as availability, solubility, moisture sensitivity of metal alkoxide, and reactivity with hydroxyl group of support.

2.1.2.4. Precipitation

Precipitation is one of the commonly used methods for making catalysts. The procedure involves precipitation from a mixture of more than two solutions or suspensions of material. The principle of precipitation is that the reaction between aqueous metal salt and basic solution (such as ammonium hydroxide, or ammonium carbonate) produces insoluble metal hydroxide or carbonate. Several advantages of precipitation method are: producing more homogeneous mixing of catalyst ingredients, homogeneous distribution of active phase throughout bulk and surface of catalyst, suitable for preparing high loading catalyst, and controllable pore size and distribution. However, there are disadvantages when two or more metal compounds are precipitated in different rate or sequence rather than simultaneously and some of the active phase will be unavailable to the surface due to being encapsulated by other material [2].

2.2. Bulk Characterization

2.2.1. Surface Area Measurement (BET)

The adsorption of a particular molecular species from a gas or liquid phase onto the surface of a solid is the principal method for measuring the total surface area of porous structures. If one can control the conditions of monolayer coverage and calculate the cross section of the molecule, then the surface area of a sample can be obtained from the volume of the adsorbed molecules. The molecules used for measuring surface area should be inert, small, spherical and easy to handle at the required temperature. Though not spherical, N_2 is usually used since it is cheap and readily available in high purity. For measuring the surface area of solid materials, nonspecific physical adsorption is required. Physical adsorption isotherms have been classified into five groups by Brunauer, Deming, Deming, and Teller (called BDDT classification) [10] (Figure 2.3). Type I (Langmuir type) is commonly found for activated carbons, silica gels, and zeolites that contain micropores (< 10 Å). Type II (sigmoid) is found for nonporous structures. Complete monolayer coverage is achieved at point B. Type III is found for systems having weak adsorption forces (e.g. water vapor on graphite). Type IV is a typically found for porous materials. The adsorption isotherm increases significantly at higher P/P_0 ratio due to pore condensation. Type V is similar to Type III with pore condensation at high P/P_o ratio. Type III and V are relatively rare and difficult to use for surface area determination due to multilayer formation before completing monolayer coverage.



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The five types of adsorption isotherms (From Satterfield, C. N. Heterogeneous (Jatalysis in Practice; McGraw-Hill: New York, 1980). Figure 2.3.

The most common method for measuring the surface areas of catalyst is that developed by Brunauer, Emmett, and Teller (called the BET method) [11]. They extended the Langmuir mechanism [12] to multimolecular layers. Langmuir assumed that an adsorption site on the solid surface accommodates one adsorbed molecule and the adsorption sites are uniform regardless of surface coverage, so that the adsorption probability (heat of adsorption) is the same at all sites. He also proposed that the rate of evaporation equals the rate of condensation for the first layer under equilibrium condition. For multimolecular layers, Brunauer, Emmett, and Teller assumed that the adsorption rate was proportional to the vacant sites of the lower layer and that the desorption rate was proportional to the adsorbed molecules in that layer. They also assumed that the heat of adsorption for all layers except the first one is equal to the heat of condensation of the molecule. The summation over an infinite number of adsorbed layers gives the following equation;

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_o}$$
(2)

where V is the volume of gas adsorbed at pressure P, V_m is the volume of gas adsorbed in monolayer, P_o is the saturation pressure of adsorbate gas at the experimental temperature, C is a constant related exponentially to the heats of adsorption and condensation of the gas. The BET equation yields a straight line when P/V(P_o-P) is plotted versus P/P_o. The BET plot is usually found to be linear in the range P/P_o = 0.05-0.35, and this range is usually used for surface area measurements. The deviation from linearity increases at higher P/P_o values (> 0.35) due to multilayer adsorption and/or pore condensation. The experimental error increases at lower P/P_o (< 0.05) due to the small amount of molecules adsorbed. The slope (S) is expressed as

$$S = \frac{(C-1)}{V_m C},$$
(3)

and the intercept (I) is expressed as

$$I = \frac{l}{V_m C}$$
(4)

Solving the equations (3) and (4) for V_m gives

$$V_{m} = \frac{1}{S+I}$$
(5)

The surface area of the catalyst can be calculated from V_m if the cross sectional area of an adsorbed molecule is known. Practically, the BET measurement can be performed with the value of the weight adsorbed on the sample (W & W_m) instead of volume (V & V_m) [13]. From the PVT relationship the amount of adsorbate adsorbed on the sample can be calculated from calibrated integrator counts caused by thermal desorption of the adsorbate.

$$W = \frac{A}{A_{cal}} V_{cal} \frac{PM}{RT}$$
(6)

where W is the mass of adsorbate adsorbed on the sample, A is the sample integrator counts, A_{cal} is the calibration integrator counts, V_{cal} is the calibration volume (cm³), P is the ambient pressure, M is the adsorbate molecular weight (g), R is the gas constant (82.1 mL atm deg⁻¹ mol⁻¹). Therefore equation (2) and (5) can be rewritten as

$$\frac{P}{W(P_o - P)} = \frac{1}{W_m C} + \frac{(C - 1)P}{W_m C P_o}$$
(7)

$$W_m = \frac{1}{S+I}$$
(8)

The total surface area of the sample (S_t) is determined from following equation;

$$S_{t} = \frac{W_{m} N A_{cs}}{M}$$
(9)

where W_m is the weight of adsorbate adsorbed at a coverage of one monolayer, N is Avogadro's number (6.02 × 10²³), A_{cs} is the cross sectional area of adsorbate molecule (N₂ = 0.162 nm²), M is the adsorbate molecular weight (g). The specific surface area S is given by following equation

S

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$$S = \frac{S_t}{\text{weight of sample (g)}}$$
(10)

2.2.2. Electron Spin Resonance (ESR)

Electron spin resonance (electron paramagnetic resonance or electron magnetic resonance) can be applied only to paramagnetic species such as supported metal ions, surface defects, adsorbed molecules, and ions on heterogeneous catalysts. In ESR, different energy states arise from the interaction of the unpaired electron spin moment with the applied magnetic field (Zeeman effect). The Zeeman Hamiltonian (\mathcal{X}) for the interaction of an electron with the magnetic field is given by following equation [14];

$$\mathcal{H} = g \beta H S_z \tag{11}$$

where g is the gyromagnetic value for a free electron (2.0023193), β is the electron Bohr magneton ($e\hbar/2m_ec$), S_z is the spin operator, and \mathcal{X} is the applied field strength. In the absence of an applied magnetic field, the electrons are oriented at random. However, under applied magnetic field, the electron spin axes are oriented either in the same direction (+) or in the opposite direction (-) with respect to H. Therefore, there are two spin populations: electron spin of $m_s = -1/2$ and $m_s = 1/2$ has lower and higher energy state respectively (Figure 2.4). The transition energy difference is given as [14]



Figure 2.4. Energy level splitting of the electron produced by an applied magnetic field.

$$\Delta \mathbf{E} = \mathbf{h} \, \mathbf{v} = \mathbf{g} \, \boldsymbol{\beta} \, \mathcal{H} \tag{12}$$

The EPR experiment usually is performed by sweeping the magnetic field at fixed frequency. When the energy difference of two states (ΔE) matches with the hv, electrons spin flip from the antiparallel to parallel. This point is called the resonance condition at which energy absorption occurs. Since absorption curves are weak, EPR spectra are usually represented as a derivative curve. The microwave frequency region such as X-band (~ 9.5 GHz) and Q-band (~35 GHz) frequency ranges are commonly used in ESR. Water has to be avoid for ESR measurement due to strong absorption of microwave. Quartz sample tube is preferred to Pyrex one because Pyrex absorb more microwave and also exhibit an EPR signal.

In this study, ESR has been used for semi-quantitative analysis for copper ions in Cu/Al_2O_3 catalysts. ESR selectively detects isolated Cu^{2+} in Cu/Al_2O_3 catalysts. Although clustered and crystalline CuO have paramagnetic Cu^{2+} ions, their resonance absorption is too broad to be detected due to the interaction with neighbor copper ions. The number of spins can be obtained by the ratio of catalyst sample to the standard signal based on following equation [15];

$$n_{u} = \frac{(A_{u}/A_{s})(g_{s}/g_{u})^{2} n_{s}}{\rho L} \frac{S_{s}(S_{s}+1)}{S_{u}(S_{u}+1)}$$
(13)

where n_u and n_s are the number of spins per gram, A_u and A_s are the areas of resonance absorption curves of sample and standard, g_u and g_s are the g values, S_u and S_s are total spins of sample and standard respectively, ρ is the mass per unit length of sample in the sample tube, and L is experimental factor. Therefore, the intensity ratio of sample vs. standard is proportional to the absolute number of spins per gram sample.

Crystalline CuSO₄•5H₂O or phosphorous doped silicon embedded in polyethylene are usually used for intensity standards. In our work, a Ruby crystal standard was glued at the center of the inside cavity for improved accuracy, because each loading of the cavity will slightly alter the standing wave of the microwave field. However, the greatest source of error usually comes from double integration of the experimental derivative curve due to the difficulty in determinating the base line. Measuring peak to peak distance was adapted in this work rather than double integration since both methods showed very similar trends.

2.2.3. X-Ray Diffraction (XRD)

2.2.3.1. Qualitative analysis of XRD

X-rays are sufficiently energetic to penetrate solid, and are well suited to probe their internal structure by diffraction. XRD is used to identify bulk crystalline phases, to quantify the amount of the crystalline phase, and to estimate particle sizes that are large enough to be detected. When an X-ray source target (e.g. Cu) is bombarded with high energy electron, the Cu K_a line (8.04 keV, 0.154 nm) is irradiated because a primary electron creates a hole in the K shell which is filled by an electron from the L shell with emission of an X-ray photon. The K_{β} line is also observed due to the electron transition from the M-shell to the K-shell. X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice. When X-rays are scattered by the ordered environment in a crystal, interference (both constructive and destructive) takes place among the scattered rays because the distances between the scattering centers are of the same order of magnitude as the wavelength of the radiation. Figure 2.5 shows how diffraction of X-rays by crystal planes allows one to derive lattice spacing by using the Bragg equation [16]

$$n \lambda = 2 d \sin(\theta)$$
(14)

where n is the integer order of the reflection, λ is the wavelength of the X-ray, d is the distance between two lattice planes, θ is the angle between the incoming X-rays and the normal to the reflecting lattice plane.

The XRD pattern is obtained with a stationary X-ray source and a movable detector. XRD peaks appear to be reflected from the crystal only if the angle of incidence for the X-ray satisfies the condition $\sin\theta = n\lambda/2d$. At all other angles, destructive interference occurs. If one measures peak positions as the angle 2 θ (which is angle between the incoming and the diffracted beams) from a XRD pattern, the Bragg equation gives the corresponding lattice spacing, which are unique characteristic for a crystal compound. For powder sample such as catalyst sample, which randomly oriented crystalline particle, only a small portion of powder sample will be oriented by chance to provide a right angle with the incident beam for constructive interference. The limitation



Figure 2.5. Constructive interference of scattered X-rays from crystalline lattice.

of XRD is that diffraction peaks are only observed when the sample contains large enough crystalline particles. If the sample contains amorphous phase or very small crystalline particle size (less than 3 nm), no diffraction peaks will be observed due to destructive interference in scattering directions where the X-rays are out of phase [17].

2.2.3.2. Quantitative analysis of XRD

In our work, quantitative X-ray diffraction data were obtained by comparing metal oxide (e.g. $CuO<\overline{111}$, $Cr_2O_3<104>$, and $CuCr_2O_4<311>$) vs. support (Al₂O₃<400>) intensity ratios measured for catalyst samples with intensity ratios measured for the physical mixtures of pure CuO, Cr_2O_3 , or $CuCr_2O_4$ and γ -Al₂O₃. For the Ce/Al₂O₃ catalyst, the CeO₂ <111> vs. Al₂O₃<440> intensity ratio was used because the Al₂O₃<440> peak is distorted severely by the CeO₂ <220> peak at high loading. Pure CuO, Cr_2O_3 , CeO₂ or CuCr₂O₄ were finely grounded before measuring XRD intensities for preparation of calibration curves (intensity ratio vs. weight percent of standard compounds based on alumina). For maximum accuracy, the sample and the standard compound peak widths (full width at half maximum) should be comparable. This method assumes that metal oxides do not disrupt the γ -Al₂O₃ spinel and do not affect the intensity of the Al₂O₃ XRD line. The error in this method is estimated to be ± 20 %.

Another quantitative XRD method compares the metal oxide (e.g. CuO) intensity relative to the metal oxide intensity for physical mixtures of pure CuO and γ -Al₂O₃. This method does not use the Al₂O₃ peak as an internal standard. It assumes that the XRD intensity is proportional to the mass of CuO. This method may be more accurate when
supported metal oxide absorbs X-ray significantly, such as at high loading of transition metal or lanthanide element.

2.2.3.3. Particle size determination

The width of diffraction peaks carries information on the dimension of the reflecting planes. Perfect crystals produce very narrow diffraction lines. However, line broadening occurs for small size crystallites (< 100 nm) due to incomplete constructive or destructive interference. The mean crystallite sizes (\overline{d}) of the crystal particles can be determined from XRD line broadening measurements using the Scherrer equation [18]:

$$d = K \lambda / \beta \cos \theta \tag{15}$$

where λ is the X-ray wavelength (Cu K_a = 0.154 nm), K is the particle shape factor, taken as 0.9. The dimension \overline{d} is defined as the effective thickness of the crystallite in a direction perpendicular to the reflecting planes. On the basis of this definition there is only a small dependence of K upon the crystallite shape. β is the full width at half maximum in radians. θ is the angle between the beam and normal on the reflecting plane (half of 2 θ).

The detection limit of XRD technique depends on the X-ray source (target material). According to the Bragg (14) and Scherrer equations (15), if one use X-ray with smaller wavelength, the λ and θ terms become smaller. Therefore, smaller particles (\overline{d}) can be detected. For example, XRD patterns from smaller particles can be obtained using a Ag (0.056 nm) or Mo (0.071 nm) target compared to Cu (0.154 nm). Another way to

improve the XRD technique is to use synchrotron radiation source. The advantages are high intensity of radiation, better signal to noise, shorter collection time and varying wavelength of X-ray. The best resolved XRD patterns can be obtained by avoiding incident radiation energy close to absorption edge of element, because the scattering efficiency of an element decreases close to an absorption edge [17].

It must be noted that while X-ray line broadening measurements are useful as a relative measure of average crystallite size, the Scherrer formula should not be used for absolute determinations due to its failure to account for the effects of microstrain, the consequences of particle size distribution, and the uncertainty in correcting for instrumental broadening [19]. Hence, the values are meant to be used for relative comparisons only.

2.3. Surface Characterization

2.3.1. Ultrahigh Vacuum Chamber

Electron spectrometers must operate under a vacuum of 10^{-6} Torr or lower. At pressures higher than 10^{-6} Torr, the electrons would be scattered in the path from the sample to the detector and the surface to be analyzed could be contaminated by gaseous impurities. A reasonable criterion for proper working pressure would be that no more than a few percent of an atomic layer of gaseous atoms should attach to the surface from the gas phase during measurement. From the simple kinetics theory of gases, the rate of arrival can be expressed as follows [20],

$$r = N \left(\frac{RT}{2\pi M}\right)^{\frac{1}{2}} = \frac{3.51 \times 10^{22} \,\mathrm{P}}{\sqrt{TM}}$$
(16)

where r is particle flux (molecules $cm^{-2}s^{-1}$), N is the number of gas molecules per cm^{3} , R is the gas constant, P is a pressure (Torr), T is a temperature (K), and M is a molecular weight. If we assume that a monolayer consists of approximately 10^{15} atoms cm^{-2} on a solid surface and the gas molecule sticking coefficient is 1, at least 10^{-9} Torr is necessary to keep the surface clean for an hour.

The ultrahigh vacuum (UHV) chamber used in our work (Figure 2.6) is pumped by a rough pump (Varian SD-90, 1.5 L/s pumping speed), a turbo molecular pump (Varian V-80, pumping speed 80 L/s), and an ion pump (Perkin-Elmer 207-0230, pumping speed 220 L/s) in combination with a titanium sublimation pump [20]. The typical base pressure of the chamber is normally approximately 1×10^{-8} Torr.

2.3.2. Transmission Electron Spectroscopy (TEM)

The TEM instrument is very similar to an optical microscope, if one replaces the optical lenses by electromagnetic ones. TEM is able to observe the size and shape of



Figure 2.6. Schematic drawings of XPS chamber.



Figure 2.7. Diagram of electron beam interaction with a solid sample.

particles directly. In TEM, a primary electron beam of high energy and intensity passes through condenser lenses to control the size of the beam that impinges on the sample, which is subsequently magnified by the objective lenses to produce a image. The interaction of a high energy electron beam with a solid sample produces various electrons and X-rays (Figure 2.7). The intensity of transmitted electrons (unscattered electrons), which depends on the density and thickness of the sample, produces a two-dimensional image of the atomic mass. Diffracted electrons formed by the elastic scattering of the electron beam by the atoms in the specimen enable one to identify crystallographic phases of the sample as well as dark field images. If an area of a sample is crystalline, scattering occurs regularly, giving a pattern of sharp spots. Polycrystalline samples produce sharp lines consisting of spots. If an area of a sample is amorphous, the pattern will contain several diffuse rings. Backscattered electrons are formed from colliding electron beams with atoms in the sample and scattering the electrons backward. Secondary electrons are formed from several consecutive inelastic collisions. X-rays and Auger electrons are formed from the relaxation of core ionized atoms and reveal information on the sample composition. The emissions of photons ranging from UV to IR are mainly caused by recombination of electron-hole pairs in the sample. Typical operating conditions of a TEM instrument are 100-200 keV electrons, 10⁻⁶ Torr, 0.5 nm resolution and a magnification of 10^{5} - 10^{6} [17].

2.3.2.1. Instrumentation for TEM

Figure 2.8 shows the TEM column used in this study. The electron gun chamber commonly consists of a tungsten wire filament, shield, and anode.



Figure 2.8. TEM column (From Flegler, S. L.; Heckman, Jr. J. W.; Klomparens, K.
 L. Scanning and Transmission Electron Microscopy: An Introduction;
 W. H. Freeman and Company: New York, 1993.

The electrons produced by the heated tungsten filament are accelerated by the potential difference between the filament and anode, which is normally 20 - 100 kV. In this study, TEM images and selected area diffraction patterns were obtained with a JEOL 100CX2 using 120 kV primary voltage. The condenser-lens system is used to control electron illumination on the sample and viewing screen. The first condenser lens can condense the 50 µm electron beam, which is the diameter of electron beam at crossover in electron gun chamber, to 1 µm. The second condenser lens is used to control the beam brightness for image viewing and photography. The objective lens, the diffraction lens, the intermediate lens, and the projector lens all contribute to image magnification. The objective lens is the first magnifying lens and the sample is inserted into it. The diffraction lens is used for imaging diffraction patterns. The intermediate lens actually magnifies image by changing intermediate lens current. The projector lens projects the final magnified the image onto the viewing screen. Apertures are a piece of metal with a small hole, typically 30 - 1000 um, depending on their function. The various apertures are used to control the electron beam diameter or to remove stray or widely scattered electrons [21].

2.3.2.2. Sample Preparation for TEM

Generally, a thin copper grid (3 mm diameter, 50 μ m thick) is used as a standard sample support disk for TEM measurements. The powder form of a catalyst sample is dispersed in water or organic solvent by an ultrasonic vibrator. In this work, methanol was used as a liquid media to prepare samples. A drop of the suspension was deposited on a holey carbon film coated copper grid and allowed to adsorb for about a minute. The

bulk of the solution was blotted off the edge of the drop with filter paper. The sample was ready for viewing after drying excess solution in the air.

2.3.3. X-Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS or ESCA) is a powerful surface sensitive techniques which provides chemical or physical information about surface atoms within about 50-100 Å thickness. From XPS measurements of heterogeneous catalysts, we can determine the oxidation state of surface atoms, dispersion of catalyst on the support, and quantitative analysis of all elements except H and He [22].

2.3.3.1. Qualitative Analysis by XPS

The primary process of XPS is an ionization phenomenon brought about by photons, the so-called photoelectric effect (Figure 2.9). A photon with energy (hv) penetrates the surface and is absorbed by atoms. An electron with binding energy (E_b) below the Fermi level escapes from the solid surface with a discrete kinetic energy (E_k) .

$$E_k = h\nu - E_b - \phi \tag{17}$$

where ϕ is the work function of the spectrometer. From the binding energy, which is characteristic for each element, the elements in a sample can be detected by XPS [23].



Figure 2.9. Diagram of XPS Process.

2.3.3.2. Quantitative analysis of XPS

XPS can be used as a quantitative tool for the determination of the chemical composition of the surface region of a solid. We can determine the concentration of impurities in a host material (e.g. supported catalyst) of known chemical composition. The signal intensity (I_i) observed in XPS can be expressed as follows [24],

$$I_{i} = I_{o} \eta_{i} \sigma_{i} \lambda_{T}(\varepsilon_{i}) D(\varepsilon_{i})$$
(18)

where I_0 is the X-ray flux, η_i is the density of atoms of i, σ_i is the photo excitation probability (photo ionization cross section), $\lambda_T(\varepsilon_i)$ is the mean free path (escape depth) of an excited electron with kinetic energy (ε_i) in the host, and $D(\varepsilon_i)$ is the fraction of electrons detected by the analyzer (analyzer-detection efficiency). From the above equation, we can find that the relative impurity vs. host material density as follows [25],

$$\left(\frac{\eta_i}{\eta_h}\right) = \frac{I_i \sigma_h \lambda_T(\varepsilon_h) D(\varepsilon_h)}{I_h \sigma_i \lambda_T(\varepsilon_i) D(\varepsilon_i)}$$
(19)

where η_i and η_h are the density of impurity and host atoms. The relative energy dependence of $D(\varepsilon_h)/D(\varepsilon_i)$ can be determined (usually $D(\varepsilon)$ is proportional to $1/\varepsilon$) and photoionization cross section (σ) have been reported by Scofield [26]. A method to estimate escape depths in elemental solids and compounds has been reported by Penn [25].

A calculation of $\lambda_T(\epsilon)$ for free-electron like materials (also valid for transition, noble, and rare earth metals) is as follows,

$$\lambda_{\rm T}(\varepsilon) = \frac{\varepsilon}{\left[a(\ln\varepsilon + b)\right]} \tag{20}$$

where a and b depend on the electron concentration of the host material. However, in order to obtain η_i/η_h for eqn.(18), we need only the relative energy dependence $\lambda_T(\varepsilon_h)/\lambda_T(\varepsilon_i)$. Penn [25] has suggested a simple equation which is independent of a and b.

$$\frac{\lambda_{\rm T}(\varepsilon_{\rm h})}{\lambda_{\rm T}(\varepsilon_{\rm i})} = \frac{\varepsilon_1(\ln\varepsilon_2 - 2.3)}{\varepsilon_2(\ln\varepsilon_1 - 2.3)}$$
(21)

This eqn.assumes (with ± 5 % error) that the mean free path ratio shows little or no dependence on the density parameters a and b, but is dependent on ε_h and ε_i (for ε_h , $\varepsilon_i \ge 200$ eV). Therefore, we can determine the relative impurity concentration.

2.3.3.3. Particle size determination

It has been shown by Defosse et al. [27] that one may calculate the theoretical intensity ratio I_p^o/I_s^o expected for a supported phase (p) atomically dispersed on a carrier (s). An extension of the Defosse model proposed by Kerkhof and Moulijn [28] has been used in the present investigation. They proposed that catalysts consisted of sheets of



Figure 2.10. Kerkhof and Moulijn's model of the supported catalysts.

support (dimension t) with cubic crystallites (dimension c) in between the layer structure (Figure 2.10). The photoelectron cross sections and the mean escape depths of the photoelectrons used in these calculations were taken from Scofield [26] and Penn [25] respectively. In the case of a crystalline sample, the intensity ratio can be expressed as

$$\left(\frac{I_{p}}{I_{s}}\right)_{cryst} = \left(\frac{p}{s}\right)_{b} \frac{D(\varepsilon_{p})\sigma_{p}\beta_{1}(1-e^{-\alpha})(1+e^{-\beta_{2}})}{D(\varepsilon_{s})\sigma_{s}2\alpha(1-e^{-\beta_{2}})}$$
(22)

where I_p is the intensity of the electrons from element p in the catalyst, I_s is the intensity of the electrons from element s in the support, σ_p and σ_s are photoelectron cross sections, $(p/s)_b$ is the bulk atomic ratio of the promoter and support, β_1 and β_2 are the dimensionless support thickness, and D are the detector efficiencies which may be a function of the kinetic energy (ε) of the electrons. α is dimensionless crystallite size parameter which can be calculated from following equation,

$$\alpha = c / \lambda_{pp} \tag{23}$$

where λ_{pp} is escape depth of electron from the element p in the catalyst traveling through the element p.

In the case of a monolayer catalyst, α is small. Therefore the intensity ratio can be expressed as follows,

$$\left(\frac{I_{p}}{I_{s}}\right)_{mono} = \left(\frac{p}{s}\right)_{b} \frac{D(\varepsilon_{p})\sigma_{p}\beta_{1}(1+e^{-\beta_{2}})}{D(\varepsilon_{s})\sigma_{s}2(1-e^{-\beta_{2}})}$$
(24)

 β_1 and β_2 can be calculated from the following equations,

$$\beta_1 = t / \lambda_{ss}, \ \beta_2 = t / \lambda_{ps}$$
(25)

where λ_{ss} is the escape depth of electron from support traveling through the support. λ_{ps} is the escape depth of electron from the promoter traveling through support.

We can calculate the crystalline size of supported materials with the following eqn. and eqn. (24), if λ_{pp} is known. The following eqn. is obtained from eqn. (22) and eqn. (23).

$$\frac{\left(\frac{I_{p}}{I_{s}}\right)_{crvst}}{\left(\frac{I_{p}}{I_{s}}\right)_{mono}} = \frac{(1 - e^{-\alpha})}{\alpha}$$
(26)

where $(I_p/I_s)_{crsyt}$ is a experimental data, $(I_p/I_s)_{mono}$ is a theoretical monolayer intensity ratio calculated from eqn. (24).

2.3.3.4. XPS shake up satellite peaks

Shake-up processes arise when the photoelectron excites an outer electron to a bound excited state in the atom or molecule. The photoelectron loses an amount of kinetic energy corresponding to the excitation and that appears at a higher binding energy in the spectrum. The origin of the satellite peaks is considered to be the promotion of 3d electrons to 4s and/or 4p levels [29-32] or alternatively to be a charge transfer of ligand electrons to unfilled 3d orbitals (e.g. $O 2p \rightarrow Cu 3d$ in case of CuO) [33-38]. Such transitions are not seen for Cu¹⁺ or Cu⁰ compounds. It is well known [39] that transition metal ions with unfilled 3d orbitals and completely empty 3d orbitals show satellite peaks due to shake-up, that the satellite peaks are not observed when the 3d orbitals are completely filled $(Zn^{2+} and Cu^{+})$, and that the transition is a monopole excitation, conserving molecular symmetry and parity. Taking into consideration the above facts, the explanation based on the ligand charge transfer seems more reasonable than that based on the 3d \rightarrow 4s, 4p transitions. In this study, we discussed the shake up satellites associated with the $Cu(2p_{3/2})$ level on the basis of the monopole charge transfer mechanism. Thus, the satellite structure provides information about the bonding nature of Cu^{2+} ion in the catalyst.

In order to estimate the nature of the distorted copper oxide structure, a correlation between the satellite intensity of the $Cu(2p_{3/2})$ level and the symmetry of the Cu^{2+} ion is required. The detailed structure of the satellite peaks depended on the catalyst composition. Frost et al. [29] reported that Cu^{2+} ion in a distorted octahedral symmetry $Cu(acac.)H_2O$, $Cu(NO_3)_23H_2O$, $Cu(OAc)_2$, $CuCO_3$ and $Cu(OH)_2$ show generally stronger

and well resolved satellite peaks compared with those in a distorted square planar symmetry (CuO, CuCl₂, CuBr₂). Strohmeier et al. [40] reported that the Cu $2p_{3/2}$ satellite structure of bulk CuAl₂O₄ (Cu ions in 60 % T_d and 40 % O_h sites) was more intense than that of CuO. The surface Cu²⁺ ions in Cu/Al₂O₃ catalysts at low loading (distributed 90 % in a tetragonally distorted octahedral environment and 10 % in tetrahedral environment) exhibit satellite peaks similar to CuO rather than CuAl₂O₄ [40,41,42]. It has been suggested [40] that this did not necessarily mean that well dispersed or amorphous CuO was present on the catalysts, but simply that the copper oxide surface spinel species is chemically different from CuO and CuAl₂O₄.

2.4. Catalytic Activity Measurement

The catalytic reactor system built for this study is shown in Figure 2.11. Measurement of CO and CH₄ oxidation activity was performed in a flow microreactor. Approximately 30 and 100 mg of catalysts was supported on a glass frit (70 - 100 μ m) for CO and CH₄ oxidation, respectively. The temperature was measured with a K-type thermocouple located just above the catalyst bed. The reactor was heated by a tube furnace (Lindberg) with temperature being controlled within 1 °C by an Omega CN 1200 temperature controller. Reactant gas flow rates were held constant with Brooks 5850 mass flow controllers. Product gases were analyzed with a Varian 920 gas chromatograph equipped with a TCD and interfaced to a Hewlett-Packard 3394A integrator. Samples (0.5 and 5 cc) were collected by Valco sample loops and electric actuator for CO and CH₄



Figure 2.11. Schematic of the catalytic reactor system.

Reaction products were separated on a 6 ft 60/80 mesh oxidation, respectively. Carbosieve S-II column. Reaction temperature control, sample injection into GC, integration of GC response were controlled automatically by a controller constructed in house. Prior to the first activity measurement, the catalyst was pretreated with a mixture of 5% O₂/He (99.5 % purity for O₂, 99.995% purity for He, AGA Gas Co.) stream (143 cc/min) at 350°C for 1 hr to remove any impurities adsorbed on the surface during catalyst preparation and storage. CO oxidation reactions were performed with a 80 cm³/min flow of 4.8% CO/9.8% $O_2/85.4\%$ He gas mixture (AGA, purity > 99.99%) at 100-310°C. Methane oxidation reactions were performed with a 15 cm³/min flow of 0.98% CH4/5.25% O₂/93.77% He gas mixture (AGA, purity > 99.99%) at 310-450 °C. All activity measurements were obtained under steady-state conditions at conversions less than 15%. Water produced during methane oxidation was frozen downstream from the reactor in a trap maintained below -40 °C with a mixture of ethanol and dry ice. The TCD response factor for each molecule was obtained using a standard gas mixture (Scotty II Analyzed Gases 1% CH₄, CO, CO₂, H₂, O₂ in N₂, Supelco). The relative thermal response factors for CO and CH₄ based on CO₂ are 1.14 and 1.33 respectively, which agree well with the reported values [43].

2.5. References

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Chapter 3

The Effect of Crystallinity on the Photoreduction of Cerium Oxide: A Study of CeO₂ and Ce/Al₂O₃ Catalysts

3.1. Abstract

The effect of crystallinity on the photoreduction of cerium oxide (Ce⁴⁺ to Ce³⁺) The effect of crystallinity on the photoreduction of cerium oxide (Ce⁴⁺ to Ce³⁺) The structure of CeO₂ and Ce/Al₂O₃ catalysts the selectron determined. Cerium oxide samples were prepared by calcining cerium (IV) the choxyethoxide in air at different temperatures. The structure of the resulting metal the selectron was determined using X-ray diffraction (XRD) and transmission electron the oxide obtained from calcination at 200 °C consisted primarily of the originated while the material produced at 750 °C contained large CeO₂ the oxide sample was reduced more extensively than the crystalline material during the samples showed that the amorphous Cerium oxide sample was reduced more extensively than the crystalline material during the pregnation using ammonium Ce(IV) nitrate and Ce(IV) methoxyethoxide precursors. XRD and XPS analyses of the Ce/Al₂O₃ catalyst derived from the nitrate precursor (designated "CeN") indicated that most of the cerium was present as poorly dispersed CeO₂ crystallites. The catalyst prepared using the alkoxide precursor (designated "CeA") also contained poorly dispersed cerium oxide; however, XRD data suggested that very
little of the cerium oxide phase was crystalline. The XPS Ce 3d spectrum obtained for the
CeN catalyst was typical of Ce(IV) oxide while the spectrum collected for the CeA
catalyst was similar to a Ce(III) compound. These results have been attributed to
manced photoreduction of the amorphous cerium oxide present in the CeA catalyst.

3.2. Introduction

Cerium oxide is an important component of superconductors [1,2], thin film tical devices [3,4], ceramics [5], gas sensors [6], and heterogeneous catalysts [7-13]. In any applications, knowledge of the cerium oxidation state is necessary for understanding properties of the material. For example, Tranquada et al. [1] have reported that the the termination of cerium valence in cerium doped copper oxide superconductors is portant for understanding the details of electron-pairing in these systems. The oxygen crage capabilities of CeO₂/Al₂O₃ catalysts are commonly attributed to reversible changes the cerium oxidation state [7-9,12].

X-ray photoelectron spectroscopy (XPS) is frequently used to determine the X-ray photoelectron spectroscopy (XPS) is frequently used to determine the X-ray function state of surface species. However, it is well known that many types of Cornpounds are not stable under the conditions used for XPS measurements [14,15]. Several factors such as X-ray flux [16], integrated X-ray dose [17], secondary electrons from the X-ray source [18], sample charging [19], temperature [20], and high vacuum [21] are known to be responsible for sample damage. Cerium oxide photoreduction during XPS measurements has been reported by several researchers [19,22-25]. Paparazzo et al. [24,25] attributed cerium oxide photoreduction primarily to intense heating of the sample surface. In contrast, Laachir et al. [26] found that CeO₂ samples with both low and high surface area (5 m²/g and 115 m²/g, respectively) were stable for up to four hours during XPS analysis. Dausher et al. [22] reported that a TiO₂-CeO₂ mixed wide prepared using the sol-gel method was more reduced during XPS measurement than the physical mixture of the two oxides. These seemingly inconsistent results may be due a difference in the structures of cerium oxides analyzed.

We are interested in the surface chemistry of cerium oxide materials that can be sed as chemical sensors [27] and heterogeneous catalysts [28]. XPS is widely utilized to termine the effect of preparation method and sample pretreatment on the distribution of rium oxidation states in such materials [10,13,29,30]. El Fallah et al. [19] demonstrated that ceria photoreduction could be limited by controlling X-ray beam power, irradiation trane, and sample charging. However, extended analysis times are sometimes necessary to tain reasonable quality spectra for materials with low cerium contents. This may cause change in cerium oxidation state and invalidate the results. Therefore, it is important to which types of materials are susceptible to photoreduction during XPS analysis. In this study, we have examined the effect of crystallinity on the photoreduction of cerium coxide. Amorphous and crystalline CeO₂ materials were prepared by calcining cerium(IV) methoxyethoxide in air at 200 °C and 750 °C, respectively. X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been used to determine the structure of these oxide materials. In addition, Ce/Al₂O₃ catalysts were prepared using ammonium Ce(IV) nitrate and Ce(IV) methoxyethoxide precursors. XRD and XPS have been used to
 d etermine the crystallinity, dispersion, and oxidation state of the alumina supported cerium
 xides. The structural information obtained for CeO₂ samples and Ce/Al₂O₃ catalysts has
 been correlated with the extent of cerium photoreduction observed during XPS

3.3. Experimental

Standard Materials. Cerium(III) acetylacetonate hydrate was obtained from Idrich Chemical Company, Inc. CeO₂ was prepared by calcining ammonium cerium(IV) Tatrate (Analytical Reagent, Mallinckrodt, Inc.) in air at 800 °C for 16 h. The XRD CeO₂ standard compound matched the appropriate Powder Diffraction File I = 1].

Cerium Oxide Sample Preparation. Cerium oxide samples were prepared by Cerium Oxide Sample Preparation. Cerium oxide samples were prepared by cerium alkoxide in those those the sample of the substrates at room temperature for 5 those samples were subsequently calcined in air at 200 °C and 750 °C for 36 h and 16 h, respectively. TGA and FTIR analyses indicated that cerium methosyethoxide decomposition was complete after calcination steps. Samples prepared at 200 °C and 750 °C are designated as Ce200 and Ce750, respectively.

Catalyst Preparation. Catalysts were prepared by pore volume impregnation of γ alumina (Cyanamid, γ -Al₂O₃, surface area = 203 m²/g, pore volume = 0.6 mL/g). The alumina support was finely ground (< 230 mesh) and calcined in air at 500 °C for 24 h
prior to impregnation. Catalysts were prepared using a deionized water solution of
ammonium cerium(IV) nitrate (Mallinckrodt Inc., Analytical Reagent) or an ethanol
solution of cerium(IV) methoxyethoxide (Gelest Inc., 18-20 % cerium alkoxide in
methoxyethanol). The catalyst derived from the cerium nitrate precursor (designated
CeN") was dried in air at 120 °C for 24 h and calcined in air at 500 °C for 16 h. The
atalyst prepared using the cerium alkoxide precursor (designated "CeA") was
mpregnated and subsequently dried at room temperature for 48 h in a N₂ purged glove
ag prior to further drying in air at 120 °C for 24 h and calcination in air at 500 °C for 16

BET Surface Area. Catalyst surface areas were determined using a QuantaChrome uantasorb Jr. Sorption System. Approximately 0.1 g of a catalyst sample was outgassed a N₂/He mixture (5% N₂) at 350 °C for 1 h prior to adsorption measurements. The casurements were made using relative pressures of N₂ to He of 0.05, 0.08, and 0.15 (N₂ Surface area = 0.162 nm²) at 77 K.

Electron Microscopy. Transmission electron microscopy (TEM) images and Selected area electron diffraction (SAED) patterns were obtained with a JEOL 100CX2 Using 120 kV primary voltage. Cerium oxide samples were ultrasonically dispersed in methanol and deposited on a holey carbon film supported on a conventional copper grid (300 mesh, 3 mm).

X-Ray Diffraction. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer employing Cu K α radiation ($\lambda = 1.5418$ Å). The X-ray was

perated at 45 kV and 100 mA. Diffraction patterns were obtained using a scan rate of
.25 deg/min. with divergence slit and scatter slit widths of 1°. Cerium oxide samples
rere run as powders mounted in the cavity of a circular silicon sample holder (C-12, Dow
orning). Catalysts were run as powders packed into a glass sample holder having a 20 x

1 $\leq x \ 0.5$ -mm cavity. The mean crystalline sizes (\overline{d}) of the CeO₂ particles were determined from XRD line broadening measurements using the Scherrer equation [32]:

$$d = K\lambda / \beta \cos \theta \tag{1}$$

here λ is the X-ray wavelength, K is the particle shape factor, taken as 0.9, and β is the width at half maximum (fwhm), in radians, of CeO₂ <111> and <220> lines measured r Ce/Al₂O₃ and CeO₂ samples, respectively.

Quantitative X-ray diffraction data for Ce/Al₂O₃ catalysts were obtained by mparing CeO₂ <111>/Al₂O₃<440> intensity ratios measured for catalyst samples with Cak ratios measured for physical mixtures of CeO₂ standard and γ -Al₂O₃ support. This thod assumes that cerium addition does not disrupt the γ -Al₂O₃ spinel and subsequently affect the intensity of the Al₂O₃ peak. The error in this method was estimated to be ± 20 .

XPS Analysis. XPS data were obtained using a Perkin-Elmer Surface Science instrument equipped with a magnesium anode (1253.6 eV) operated at 300 W (15 kV, 20 mA) and a 10-360 hemispherical analyzer operated with a pass energy of 50 eV. The irnstrument typically operated at pressures near 1 x 10⁻⁸ Torr in the analysis chamber. The take-off angle between the sample and analyzer was approximately 45° for all receiver and sample was maintained at Deproximately 3/4 inch for all analyses. Spectra were collected using a PC137 board **i** refaced to a Zeos 386SX computer. CeO₂ samples were analyzed as prepared while Catalyst samples were analyzed as powders dusted onto double-sided sticky tape or spray control a quartz slide using a methanol suspension of the catalyst. XPS binding \leftarrow regies were measured with a precision of ± 0.2 eV, or better. Binding energies for the **S** and ard samples were referenced to the C 1s line (284.6 eV) of the carbon overlayer. S ince the charging observed for the Ce200 and Ce750 samples changed during our \sim periments, we were concerned that the C ls charge reference may be less accurate than Ce 3d derived charge correction. Thus, we have charge corrected the Ce 3d spectra 3 **Solution** the cerium oxide samples using the Ce 3d u'' peak (916.7 eV). Using the Ce \rightarrow d u" reference energy, the binding energy of the C ls peak measured for the CeO₂ Standard was 284.6 eV. The Ce 3d u'' peak has been commonly used to compensate for Sample charging in the ceria photoreduction studies [19,24,25]. Binding energies for the **Catalyst samples were referenced to the Al 2p peak (74.5 eV) of the alumina support.** The **C**e 3d spectra of Ce200 and Ce750 samples were obtained at 15 min. intervals up to 300 min. The Ce 3d region of CeN and CeA catalysts were measured for 600 min. to obtain reasonable quality spectra. The extent of cerium reduction was determined using composite spectra [33] derived from the Ce 3d spectra measured for CeO₂ and Ce(III) acetylacetonate hydrate standard compounds. We estimate the error in this method is less than ± 5 %.

Quantitative XPS Analysis. It has been shown by Defosse et al. [34] that one may calculate the theoretical intensity ratio I_p^o/I_s^o expected for a supported phase (p) atomically dispersed on a carrier (s). An extension of the Defosse model proposed by Kerkhof and Moulijn [35] has been used in the present investigation. The photoelectron cross sections and the mean escape depths of the photoelectrons used in these calculations were taken from Scofield [36] and Penn [37], respectively. For a phase (p) present as discrete particles, the experimental intensity ratio (I_p/I_s) is given by the following expression:

$$I_{p}/I_{s} = I^{o}_{p}/I^{o}_{s} \left[1 - \exp\left(-d/\lambda_{p}\right)\right] / d/\lambda_{p}$$
(2)

where (I_p^o/I_s^o) is the theoretical monolayer intensity ratio, d is the length of the edge of the cubic crystallites of the deposited phase and λ_p is the mean escape depth of the photoelectrons in the deposited phase.

3.4. Results and Discussion

XPS Analysis of Standard Compounds. The XPS Ce 3d spectra of cerium compounds are known to be complicated due to hybridization of the Ce 4f with ligand orbitals and fractional occupancy of the valence 4f orbitals [38-44]. Figure 3.1 shows the



Figure 3.1. Ce 3d XPS spectra measured for (a) CeO₂ and (b) Ce(III) acetylacetonate hydrate.

Ce 3d spectra measured for CeO₂ and Ce(III) acetylacetonate hydrate standard compounds. The peak shapes are similar to those reported for Ce(IV) and Ce(III) compounds [10,29,45,46]. The Ce 3d spectrum measured for CeO₂ contains three main $3d_{5/2}$ features at 882.6 eV (v), 889.3 eV (v"), and 898.6 eV (v") and three main $3d_{3/2}$ features at 900.8 eV (u), 907.8 eV (u"), and 916.7 eV (u"). The high binding energy doublet v"(u") has been assigned to a final state with primarily $4f^0$ configuration. The v" and v (u" and u) doublets are generally assigned to final states with strong mixing of $4f^4$ and $4f^2$ configurations. These states arise from the core hole potential in the final state and 4f hybridization in the initial state [38-43]. The Ce 3d spectrum measured for Ce(III) acetylacetonate hydrate contains two main $3d_{5/2}$ peaks at 881.4 eV (v) and 885.2 eV (v') and two main $3d_{3/2}$ features at 899.5 eV (u) and 903.6 eV (u'). These doublets have been assigned to final states where $4f^4$ and $4f^2$ configurations are strongly mixed [44].

Structure of Ce200 and Ce750. TEM images and SAED patterns of Ce200 and Ce750 samples are shown in Figure 3.2. The micrograph obtained for the Ce200 sample consists of thick agglomerates with no preferred shape or orientation; however, small grains (~ 3 nm diameter) are observed at the edges of agglomerates. The SAED pattern of the Ce200 sample shows several diffuse rings indicative of an amorphous phase. The TEM image obtained for the Ce750 sample shows faceted particles. The SAED pattern shows several sets of sharp spots characteristic of a crystalline phase.

Figure 3.3 shows the XRD patterns obtained for Ce200 and Ce750 samples. The most intense CeO₂ peak (CeO₂ <111>) was excluded from this figure due to overlap with a broad silica peak from the sample substrate. The XRD pattern obtained for the Ce200



(a)









Figure 3.2. TEM micrographs and SAED patterns obtained for (a) Ce200 and (b) Ce750 samples.

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Figure 3.3. XRD patterns measured for (a) Ce200 and (b) Ce750 samples.
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sample shows broad, weak peaks characteristic of poorly crystallized CeO₂. The diffraction pattern measured for the Ce750 sample shows more intense, sharper CeO₂ peaks. In addition, the CeO₂ <222> peak can be observed in the diffraction pattern of the Ce750 sample. CeO₂ particle sizes determined using XRD line broadening calculations are significantly larger for the Ce750 sample (34.8 nm) than for the Ce200 sample (2.2 nm). For the Ce200 sample, the XRD determined CeO₂ particle size is similar to the grain size observed in TEM.

In summary, TEM and XRD results indicate that calcination of cerium alkoxide leads to the formation of cerium oxide. The extent of crystallinity is affected by the calcination temperature. The Ce200 sample consists primarily of large, amorphous cerium oxide particles that contain small CeO₂ crystallites. The Ce750 sample consists primarily of large CeO₂ crystallites. No evidence for the presence of an amorphous cerium oxide phase has been observed for the Ce750 sample.

Photoreduction of Ce200 and Ce750. Figure 3.4 shows the Ce 3d spectra measured for the Ce200 sample as a function of irradiation time. The spectrum obtained in the first 15 min. of analysis has features similar to those observed for the CeO₂ standard; the Ce $3d_{52}$ binding energy (882.7 eV) is identical, within experimental error, to the value measured for CeO₂ (882.6 eV). As the analysis time increases, new features characteristic of Ce³⁺ appear in the Ce 3d spectra. For intermediate irradiation times (30 and 60 min.), this is most evident as a loss of resolution between the v and v" peaks of Ce⁴⁺ due to the growth of the v¹ peak characteristic of Ce³⁺. We believe that the new features appearing in the Ce 3d spectrum are due to the photoreduction of Ce⁴⁺ to Ce³⁺ during the XPS analysis. This is consistent with numerous reports in the literature [19,22-25]. We also note that



Figure 3.4. Ce 3d XPS spectra measured for the Ce200 sample after irradiation times of (a) 15 min., (b) 30 min., (c) 60 min., (d) 120 min., (e) 180 min., and (f) 300 min.

increasing analysis time broadens the Ce $3d_{5/2}$ region on the low binding energy side. Paparazzo [24] has reported that such broadening can be attributed to the superposition of "Ce₂O₃" components and CeO₂ features. The spectrum measured after 300 min. clearly shows features characteristic of Ce³⁺ and Ce⁴⁺. The Ce $3d_{5/2}$ binding measured for the Ce³⁺ v' component (885.4 eV) in the irradiated sample is close to values measured for Ce(III) acetylacetonate hydrate (885.2 eV) and reported for Ce₂O₃ (885.3 eV [25] and 885.8 eV [47]) compound. In addition, Le Normand et al. [48] reported that a v' peak (885.5 eV) appeared in the XPS Ce 3d spectra measured for CeO₂ reduced in H₂ at 900 °C.

The XPS Ce 3d spectra measured for the Ce750 sample are shown as a function of irradiation time in Figure 3.5. One can clearly see that these spectra also change with time; however, the growth of Ce^{3+} features is less dramatic than those observed for Ce200 sample. The XPS Ce 3d binding energies measured for the Ce750 sample are identical, within experimental error, to the values obtained for the Ce200 sample. For the Ce750 sample, well resolved v and v" peaks are observed for the duration of the experiment.

Figure 3.6 shows the extent of cerium reduction with respect to irradiation time for Ce200 and Ce750 samples. As anticipated from Figures 3.4 and 3.5, the extent of reduction increases rapidly with time up to approximately 180 min. For longer analysis times, the change in fraction reduced is less pronounced. This indicates that the rate of reduction decreases with irradiation time. Similar results have been reported by Wallbank et al. [49] in the case of CuF₂ photoreduction (Cu²⁺ to Cu⁰). Figure 3.6 also shows that the cerium oxide calcination temperature affects the extent of reduction. As noted above,



Figure 3.5. Ce 3d XPS spectra measured for the Ce750 sample after irradiation times of (a) 15 min., (b) 30 min., (c) 60 min., (d) 120 min., (e) 180 min., and (f) 300 min.



Figure 3.6. Fraction of CeO₂ reduced as a function of irradiation time for the Ce200 (O) and Ce750 (●) samples.

TEM and XRD analyses have shown that the Ce200 sample consists of small CeO₂ crystallites imbedded in large amorphous cerium oxide particles, while the Ce750 sample contains only large CeO₂ crystallites. Thus, we believe the photoreduction results indicate that amorphous cerium oxide is more readily reduced than crystalline CeO₂ during the XPS measurement.

Structure of Cerium/Alumina Catalysts. The surface areas of CeN and CeA catalysts (195 m²/g) are identical and slightly lower than the value obtained for the Al₂O₃ support (203 m²/g). Figure 3.7 shows the XRD patterns obtained for CeN and CeA catalysts. The XRD pattern of the CeN catalyst shows intense peaks characteristic of CeO₂; however, only weak CeO₂ lines are observed in the diffraction pattern of the CeA catalyst. Quantitative XRD measurements indicate that the CeN catalyst contains 4.6 wt.% crystalline CeO₂ phase, while the CeA catalyst contains only 0.3 wt.% crystalline CeO₂.

Variation in the particle size of the cerium oxides determined from XRD line broadening calculations and XPS Ce/Al intensity ratios are shown in Table 3.1 for both CeN and CeA catalysts. The CeO₂ particle size determined for the CeN catalyst using XRD is slightly larger than the value obtained for the CeA catalyst. However, the CeO₂ particle size calculated from XRD analysis of the CeA catalyst must be considered as approximate due to the low intensity of the CeO₂ <111> peak. The cerium oxide particle sizes determined for CeN and CeA catalysts using XPS intensity ratios are identical and smaller than the values obtained from XRD.



Figure 3.7. XRD patterns measured for (a) alumina support and (b) CeA and (c) CeN catalysts.

In summary, XRD and XPS analyses indicate that the cerium oxide dispersion is similar for catalysts derived from nitrate (CeN) and alkoxide (CeA) cerium precursors. However, the CeN catalyst consists primarily of CeO₂ crystallites while most of the cerium oxide present in the CeA catalyst is amorphous [28].

	Particle Size (nm)		
Samples	XRD	XPS	
CeN	5.1	1.6	
CeA	4.5	1.6	

Table 3.1.Particle Sizes of Cerium Oxide Species in Ce/Al2O3Catalysts Determined from XRD Line Broadening
and XPS Intensity Ratios Measurements.

Photoreduction of Cerium Alumina Catalysts. Figure 3.8 shows the Ce 3d spectra obtained for CeN and CeA catalysts. The XPS Ce 3d spectrum measured for the CeN catalyst shows Ce^{4+} and Ce^{3+} features similar to those observed for the photoreduced Ce750 sample. For the CeA catalyst, the Ce 3d spectrum has v' and u' lines similar to those observed for the Ce(III) acetylacetonate hydrate standard compound as well as the u''' peak associated with Ce⁴⁺ species.

The presence of Ce^{3+} in calcined Ce/Al_2O_3 catalysts is often attributed to the formation of bulk CeAlO₃ or a Ce-Al₂O₃ surface phase. We do not believe that the CeN and CeA catalysts examined in this study contain either of these species since they were prepared using Ce⁴⁺ precursors and were calcined at a relatively low temperature. Shyu et



Figure 3.8. Ce 3d XPS spectra measured for (a) CeN and (b) CeA catalysts.

al. [29] have reported that high temperature (1000 °C), long reaction times (80 h), and a reducing atmosphere were required to form bulk CeAlO₃ in Ce/Al₂O₃ catalysts. Formation of a Ce³⁺-Al₂O₃ surface phase would seem to require a Ce³⁺ precursor. Further, the relatively poor Ce dispersion noted for CeN and CeA catalysts is not consistent with the formation of a Ce-Al₂O₃ surface phase since surface phases are normally considered to be highly dispersed (particle size < 1 nm). Thus we believe that the Ce³⁺ species observed by XPS arise from cerium oxide photoreduction. The greater extent of photoreduction shown by the CeA catalyst can be attributed to the predominance of amorphous cerium oxide in the catalyst.

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Chapter 4

The Influence of Surface Structure on the Catalytic Activity of Alumina Supported Copper Oxide Catalysts: Oxidation of Carbon Monoxide and Methane

4.1. Abstract

X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and electron spin resonance (ESR) have been used to characterize a series of Cu/Al₂O₃ catalysts. The information obtained from surface and bulk characterization has been correlated with CO and CH₄ oxidation activity of the catalysts. For catalysts with Cu/Al atomic ratios \leq 0.051, XPS data indicated that most of the Cu was present as a dispersed surface phase. ESR results showed that the ratio of isolated/interacting copper surface phase decreased with increasing Cu content. For catalysts with Cu/Al atomic ratio \geq 0.077, large CuO crystallites were detected by XRD. The turn over number for CO oxidation increased with increasing Cu content. This has been attributed to an increase in the amount of crystalline CuO present in the catalysts. The specific activity for CH₄ oxidation decreased with increasing Cu content up to Cu/Al = 0.051. XPS results indicate that Cu dispersion decreased with increasing Cu content. Since the turn over number has been exidat prepe intera for th contr of C([15,1 exide ativi 007.Dr emiss œlcir HAI2 SUSCE in the Cup (the in oxidation activity could not be attributed to a decrease in Cu dispersion. Instead, we propose that the isolated Cu surface phase is more active for CH_4 oxidation than the interacting copper surface phase or crystalline CuO. CH_4 oxidation activities were similar for the catalysts with Cu/Al atomic ratio ≥ 0.077 .

4.2. Introduction

Copper oxide is one of the most active transition metal oxide catalysts for emission control reactions [1-9]. Catalysts based on copper oxide are useful for the total oxidation of CO [5,6,10-12], hydrocarbons [2,5,6,13], chlorinated hydrocarbons [14], and alcohols [15,16]. NO_x [7,17-19] and SO₂ reduction [19] reactions are also catalyzed by copper oxide. Kummer [2] has reported that copper oxide catalyst exhibits a CO oxidation activity per unit surface area similar to that of noble metal catalysts. Thus, supported copper oxide catalysts have been considered as suitable substitutes for noble metal-based emission control catalysts.

The structure of Cu/Al₂O₃ catalysts depends on both the metal loading and calcination temperature [20-32]. For low copper loadings (< 8~10 wt.% Cu on 200m²/g γ-Al₂O₃ support), copper is present as a well-dispersed surface phase. Magnetic susceptibility and ESR measurements have been used to distinguish between two species in the copper surface phase: isolated and interacting copper species [20-25]. The isolated cupric ions contribute to both magnetic susceptibility and resonance absorption, whereas the interacting copper species (or 'clustered copper ions') do not give a detectable ESR

signal. The copper surface spinel is believed to result either from the diffusion of copper ions into an alumina lattice [26] or from the interaction of a Cu^{2+} ion complex with alumina hydroxyl groups [28]. Strohmeier et al. [26] have reported that the chemical state of the spinel is different from both bulk CuO and CuAl₂O₄. Indeed, diffuse reflectance spectroscopy results have shown that cupric ions in the surface spinel predominantly occupy tetragonally distorted octahedral sites (> 90%) with only a small fraction located in tetrahedral sites [21,29,32]. Bulk CuAl₂O₄ (60 % tetrahedral Cu²⁺ and 40 % octahedral Cu²⁺) can be formed only after high temperature calcination (> 700 °C) [20,21,26]. For high copper loadings (> 10 wt.% Cu), crystalline CuO is formed on the alumina support [21,26].

The CO and CH₄ oxidation activities of Cu/Al₂O₃ catalysts also depend on copper content. Mooi and Selwood [33] have reported that the CO oxidation activity is the highest for a 7 wt.% CuO/Al₂O₃ catalyst (supported on 200 m²/g γ-Al₂O₃). Severino et al. [10] reported that a 5 wt.% CuO/Al₂O₃ catalyst (supported on 100 m²/g γ-Al₂O₃) shows the maximum CO oxidation activity. The authors attributed the activity of the low loading catalysts to copper ions dispersed on the alumina surface. However, Pierron et al. [34] have reported that CO oxidation occurs on crystalline copper oxide phases. Tsikoza et al. [35] and Marion et al. [36,37] reported that the CH₄ oxidation activity per unit mole or gram of copper decreases with increasing copper loading. Tsikoza et al. [35] suggested that CH₄ oxidation proceeds primarily on the well-dispersed copper surface phase. **Marion** et al. [36,37] also suggested that the catalytic activity for methane oxidation depends on the amount of well-dispersed copper ions. In addition, these authors

attributed the decrease in CH₄ oxidation activity with increasing Cu loading primarily to a decrease in copper oxide dispersion.

Several previous studies of Cu/Al₂O₃ catalysts have focused on the structure or activity of the catalyst. Little effort has been devoted to investigating systematically the relationship between the surface structure and CO and CH₄ oxidation activity of Cu/Al₂O₃ catalysts. The present work is part of a broad study to investigate structure-reactivity correlations for transition metal oxide based emission control catalysts. In this paper, Xray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and electron spin resonance (ESR) have been used to determine the effect of Cu loading on the chemical state and dispersion of copper species supported on γ-alumina. The information derived from these techniques is correlated with the CO and CH₄ oxidation activity in order to develop a more complete understanding of Cu/Al₂O₃ catalysts.

4.3. Experimental

Catalyst Preparation. Catalysts were prepared by pore volume impregnation of γalumina (Cyanamid, surface area = 203 m²/g, pore volume = 0.6 mL/g) using solutions of copper(II) nitrate (Columbus Chemical Industries Inc, ACS Grade). The alumina was finely ground (<230 mesh) and calcined in air at 500 °C for 24 h prior to impregnation. The impregnated samples were dried in air at 120 °C for 24 h and calcined in air at 500 °C for 16 h. The copper content of the Cu/Al₂O₃ series was varied from a Cu/Al atomic ratio of 0 to 0.128 (0 to 20 wt.% CuO). Cu/Al₂O₃ catalysts will be designated by "Cuy",

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where y is the Cu/Al atomic ratio $(\times 10^2)$ of the catalysts. The catalyst colors change with increasing copper content from pale blue (Cu0.3 and Cu0.6), to pale green (Cu1.3 and Cu2.6), to green (Cu5.1), to dark green (Cu7.7), to gray (Cu10), to dark gray (Cu13).

Standard Materials. CuO was prepared by calcining copper(II) nitrate in air at 500 °C for 16 h. $CuAl_2O_4$ was prepared by calcining stoichiometric amounts of the respective nitrates in air at 1000 °C for 24 h. XRD patterns of the standard compounds matched the appropriate Powder Diffraction File [38].

BET Surface Area. Surface area measurements were performed using a QuantaChrome Quantasorb Jr. Sorption System. Approximately 0.1 g of catalyst were outgassed in a N₂/He mixture (5% N₂) at 350 °C for 1 h prior to adsorption measurements. The measurements were made using relative pressures of N₂ to He of 0.05, 0.08, and 0.15 (N₂ surface area = 0.162 nm^2) at 77 K. Increasing the copper content of the catalysts decreases the BET surface area by a maximum of 20 %.

X-Ray Diffraction. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer employing Cu K_a radiation ($\lambda = 1.5418$ Å). The X-ray was operated at 45 kV and 100 mA. Diffraction patterns were obtained using a scanning rate of 0.5 deg/min (in 20) with divergence slit and scatter slit widths of 1°. Samples were run as powders packed into a glass sample holder having a 20 x 16 x 0.5-mm cavity.

The mean crystallite sizes (\overline{d}) of the CuO particles were determined from XRD *line* broadening measurements using the Scherrer equation [39]:

$$d = K\lambda / \beta \cos \theta \tag{1}$$

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where λ is the X-ray wavelength, K is the particle shape factor, taken as 0.9, and β is the full width at half maximum (fwhm), in radians, of the CuO<111> line.

Quantitative X-ray diffraction data were obtained by comparing $CuO<\bar{1}11>/Al_2O_3<400>$ intensity ratios measured for catalyst samples with intensity ratios measured for physical mixtures of pure CuO and γ -Al_2O_3. This method assumed that copper addition did not disrupt the γ -Al_2O_3 spinel and subsequently affect the intensity of the Al_2O_3<400> line. The error in this method was estimated to be ± 20 %.

XPS Analysis. XPS data were obtained using a Perkin-Elmer Surface Science instrument equipped with a magnesium anode (1253.6 eV) operated at 300 W (15 kV, 20 mA) and a 10-360 hemispherical analyzer operated with a pass energy of 50 eV. The instrument typically operates at pressures near 1 x 10⁻⁸ Torr in the analysis chamber. Spectra were collected using a PC137 board interfaced to a Zeos 386SX computer. XPS spectra were also obtained using a VG Microtech spectrometer to confirm Cu 2p_{3/2} binding energies. The VG spectrometer is equipped with a magnesium anode (1253.6 eV) operated at 300 W (15 kV, 20 mA) and a Clam2 hemispherical analyzer operated with a pass energy of 50 eV. The instrument typically operates at pressures below 1 x 10⁻⁸ Torr in the analysis chamber. Samples were analyzed as powders dusted onto double-sided sticky tape or spray coated onto a quartz slide using a methanol suspension of the catalyst. Binding energies for the catalyst samples and standard compounds which contained Al were referenced to the Al 2p peak (74.5 eV). The binding energy for CuO was referenced to the C 1s line (284.6 eV) of the carbon overlayer. Detector efficiency was corrected using Cu 2p and Cu 3p peak intensities measured for copper metal foil which was cleaned with Ar ion bombardment. Since the Cu 3p line overlaps the Al 2p line for the catalyst samples, estimated Cu 3p intensities (from the ratio of Cu 3p to Cu 2p) were subtracted from Al 2p intensities prior to calculating the Cu/Al intensity ratio. XPS binding energies were measured with a precision of ± 0.2 eV, or better.

Reduction of copper species during XPS experiments has been reported [26,40,41] and attributed to several factors such as X-ray flux, X-ray dose, temperature, and pressure. In order to minimize the effect of photoreduction on the results, all samples were analyzed using the same distance between the X-ray source and sample (~ 2 cm) and minimum data acquisition time (5 min). No significant photoreduction was observed using these experimental conditions.

Quantitative XPS Analysis. It has been shown by Defosse et al. [42] that one may calculate the theoretical intensity ratio $I^{\circ}_{p}/I^{\circ}_{s}$ expected for a supported phase (p) atomically dispersed on a carrier (s). An extension of the Defosse model proposed by Kerkhof and Moulijn [43] has been used in the present investigation. The photoelectron cross sections and the mean escape depths of the photoelectrons used in these calculations were taken from Scofield [44] and Penn [45], respectively. For a phase (p) present as discrete particles, the experimental intensity ratio I_p/I_s is given by the following expression:

$$I_{p}/I_{s} = I_{p}^{\circ}/I_{s}^{\circ} \left[1 - \exp\left(-d/\lambda_{p}\right)\right] / d/\lambda_{p}$$
⁽²⁾

where I_p^o/I_s^o is the theoretical monolayer intensity ratio, d is the length of the edge of the cubic crystallites of the deposited phase and λ_p is the mean escape depth of the photoelectrons in the deposited phase. The Cu species particle sizes were determined by solving the Eq.(2) for d. The relative Cu dispersion to the monolayer was estimated from the ratio of I_p/I_s to I_p^o/I_s^o .

ESR Study. ESR spectra were obtained using a Varian E-4 spectrometer with a rectangular TE_{102} cavity operated at a microwave frequency of 9.06 GHz and a power of 20 mW. Ruby crystal mounted inside the cavity at fixed orientation was used as an intensity standard for determination of relative ESR intensities. The relative intensities per unit mg CuO were obtained from the ratio of the peak intensity of catalyst sample to the value of Ruby crystal. Powder samples were dried at 120 °C for 24 hr prior and run at 98 K in a quartz ESR tube.

CO Oxidation Activity. Measurement of CO oxidation activity was performed in a flow microreactor. Approximately 0.03 g of catalyst were supported on a glass frit (70 -100 μm) and the temperature was measured with a K-type thermocouple located just above the catalyst bed. The reactor was heated by a tube furnace (Lindberg) with temperature being controlled within 1 °C by an Omega CN 1200 temperature controller. Reactant gas flow rates were held constant with Brooks 5850 mass flow controllers. Product gases were analyzed with a Varian 920 gas chromatograph equipped with a TCD and interfaced to a Hewlett-Packard 3394A integrator. Reaction products were separated On a 6 ft 60/80 mesh Carbosieve S-II column. Prior to the first activity measurement, **Catalysts were pretreated with a mixture of 5% O₂/He (99.5 % purity for O₂, 99.995 %**

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purity for He, AGA Gas Co.) stream (143 cc/min) at 350 °C for 1 hr to remove any impurities adsorbed on the surface during catalyst preparation and storage. CO oxidation reactions were performed with a constant flow rate (80 cm³/min) of 4.8% CO/9.8% $O_2/85.4\%$ He gas mixture (AGA, purity > 99.99 %) in the temperature range of 150-400 °C.

CH₄ Oxidation Activity. Methane oxidation reactions were performed with a **CONSTRUMT** flow (15 cm³/min) of 0.98% CH₄/5.25% O₂/93.77% He gas mixture (AGA, **Purity** > 99.99%) in the temperature range of 360-430 °C. Approximately 0.1 g catalyst were charged into the same type of microreactor used for CO oxidation measurements. Water produced during methane oxidation was frozen downstream from the reactor in a **trap** maintained < -40 °C with a mixture of ethanol and dry ice. All activity measurements (CO and CH₄ oxidation) were obtained under steady-state conditions at conversions less **than** 15%. The turn over number (TON) was expressed as mole CO or CH₄ oxidized per **TO**le of surface-bound copper. The surface bound copper content was determined by **SPS** from the relative intensity ratios of Cu $2p_{3/2}$ and Al 2p peaks.

4.4. **Results**



Figure 4.1. XRD patterns measured for (a) Al₂O₃, (b) Cu7.7, (c) Cu10, and (d) Cu13.

Catalysts	Crystalline Phase (wt.%)		
-	As prepared	Measured	
Cu 0.3	0.5	0	
Cu 0.6	1	0	
Cu 1.3	2	0	
Cu 2.6	4	0	
Cu 5.1	8	0	
Cu 7.7	12	5.7	
Cu 10	16	10.8	
Cu 13	20	14.6	

Table 4.1.Concentration of Crystalline* Phases in Cuy
Catalysts Calculated from Quantitative XRD Data.

a- Valid for crystalline phases with particle sizes > 3.0 nm.

d). The intensities of the CuO XRD peaks increase with increasing Cu content. Quantitative XRD measurements (Table 4.1) show that the amount of crystalline CuO increases from 5.7 to 14.6 wt.% as the Cu/Al atomic ratio increases from 0.077 to 0.13. The XPS Cu $2p_{3/2}$ binding energies measured for the Cuy catalysts (935.1 ± 0.2 eV) were independent of Cu content and similar to the Cu $2p_{3/2}$ binding energy measured for $CuAl_2O_4$ (935.0 eV) and higher than the value measured for CuO (933.9 eV). The satellite/main peak ratio measured for the Cuy catalysts (0.47 ± 0.1) is similar to that The asured for CuO (0.45) and lower than the value for CuAl_2O_4 (0.71).

Figure 4.2 shows the variation of the Cu $2p_{3/2}$ /Al 2p intensity ratio measured for the Cuy catalysts as a function of Cu/Al atomic ratio. The theoretical line calculated for monolayer dispersion [43] is shown for comparison. The Cu/Al intensity ratio increases with increasing Cu/Al atomic ratio up to 0.051. For higher Cu loadings, the Cu/Al intensity ratio measured for the catalysts levels off. Variation in the particle size of the



Figure 4.2. Cu 2p_{3/2}/Al 2p XPS intensity ratios measured for Cuy catalysts(•) plotted versus Cu/Al atomic ratio. Cu 2p_{3/2}/Al 2p intensity ratios calculated for monolayer dispersion (line).

Catalysts	Particle size (nm)		
	XPS	XRD	
Cu 0.3	0.4	_ ^a	
Cu 0.6	0.6	- *	
Cu 1.3	0.8	_ ^a	
Cu 2.6	0.8	_ a	
Cu 5.1	0.9	_*	
Cu 7.7	1.7	30	
Cu 10	2.3	30	
Cu 13	3.0	29	

Table 4.2.Particle Size of Copper Phases Determined from
Cu/Al XPS Intensity Ratios and XRD Line
Broadening Calculations.

a- No CuO XRD peaks detected for these catalysts

copper species determined from Cu/Al XPS intensity ratios using Eq. (2) is given as a function of the Cu loadings in Table 4.2. The mean particle size of the copper species **calculated from XPS intensity ratios increases from 0.4 to 3.0 nm with increasing Cu/Al atomic ratio.** Particle sizes determined from XRD line broadening calculations using Eq. (1) are also shown in Table 4.2. For catalysts with Cu/Al atomic ratios ≥ 0.077 , XRD line **broadening calculations show that the CuO crystallite sizes are independent of Cu loading and significantly larger than the values determined using XPS.**



Figure 4.3. Normalized ESR intensity (1 mg CuO) of Cuy catalysts relative to the internal standard.

CO Oxidation		CH ₄ Oxidation		
Catalysts	Activation Energy	TON (x10 ⁴)	Activation Energy	TON (x10 ⁴)
Cu 0.3	25.8	3.5	21.8	11.8
Cu 0.6	25.7	6.8	22.1	8.3
Cu 1.3	19.2	33.6	22.6	6.5
Cu 2.6	19.4	76.0	23.4	4.7
Cu 5.1	19.2	242	21.9	2.8
Cu 7.7	13.1	390	22.3	3.2
Cu 10	13.7	694	23.6	2.9
Cu 13	13.2	1010	21.4	2.9

Table 4.3. Turn Over Numbers^a and Activation Energies^b of Cu/Al_2O_3 Catalysts for CO and CH₄ Oxidations.

a- Estimated from Arrhenius plots (kcal/mol) within 15 % conversion.

b- Calculated at 260 and 390 °C for CO and CH₄ oxidation respectively (s⁻¹) using exposed Cu species determined from XPS.

CO Oxidation Activity. Table 4.3 shows the specific turn over number (TON) for CO oxidation over Cuy catalysts calculated at 260 °C using XPS estimates of the Cu dispersion. The TON increases by nearly a factor of 300 as the Cu/Al atomic ratio increases from 0.003 to 0.13. The activation energies calculated for CO oxidation are also shown as a function of Cu content in Table 4.3. The activation energy decreases from 25.8 to 13.1 kcal/mol as the Cu/Al atomic ratio increases from 0.003 to 0.077. For Catalysts with Cu/Al atomic ratios ≥ 0.077 , the activation energies are identical within

CH₄ Oxidation Activity. Table 4.3 shows the TON for CH₄ oxidation over Cuy Catalysts calculated at 390 °C using XPS estimates of the Cu dispersion. The TON Cecreases by nearly a factor of 4 as the Cu/Al atomic ratio increases from 0.003 to 0.051. Further addition of Cu has little effect on the TON for CH₄ oxidation. Table 4.3 also shows that the activation energies calculated for CH_4 oxidation are similar within experimental error (22.4 ± 1.0 kcal/mol).

For catalysts with Cu/Al atomic ratio ≤ 0.006 , the CO₂ selectivity measured at 390 °C increased from 63 % to 80 % with increasing copper content. No partial oxidation product was observed for catalysts with Cu/Al atomic ratio ≥ 0.013 .

4.5. Discussion

Structure of Copper/Alumina Catalysts. For catalysts with Cu/Al atomic ratio \leq O. O51, the absence of XRD peaks characteristic of discrete CuO and the small particle size **calculated** from Cu/Al XPS intensity ratios suggest that copper exists as a well-dispersed **copper surface** phase. These results are consistent with previous work by Friedman et al. [21], which showed that the support capacity of several γ -aluminas for copper surface **phase** is approximately 4 wt.%Cu/100m²/g support. Strohmeier et al. [26] also reported **that** 9-10 wt.% copper (for 195 m²/g γ -alumina) is the maximum copper loading that can **be** accommodated as a surface phase.

The Cu $2p_{3/2}$ XPS spectra measured for the Cuy catalysts show Cu $2p_{3/2}$ binding ergies characteristic of CuAl₂O₄ and satellite/main peak intensity ratios close to the value obtained for CuO. It is well known [21,26] that Cu/Al₂O₃ catalysts contain Cu²⁺ surface phase and discrete CuO particles. In principle, photoelectrons from both discrete O particles and Cu²⁺ surface phase will contribute to the XPS signal. However, due to
the high dispersion of the surface phase relative to the CuO crystallites, the qualitative features of the Cu 2p_{3/2} XPS spectra are expected to be more representative of the surface phase. Consequently, the observation of satellite/main peak intensity ratios typical of CuO is surprising. However, this apparent discrepancy has been reported by previous researchers [26,30]. Strohmeier et al. [26] suggested that this did not necessarily mean that well-dispersed or amorphous CuO was present on the catalysts, but simply that the **Copper surface species is chemically different from bulk CuO and CuAl₂O₄.**

The significant decrease in the relative ESR intensity as a function of Cu content is **consistent** with the result from previous work [21,22]. The ESR result indicates that **isolated/interacting** copper surface phase ratio decreases as Cu loading is increased in the **range** of $0 < Cu/Al \le 0.051$. The former contributes the resonance absorption, which can **be** assigned as tetragonally distorted, octahedrally-coordinated cupric ions [23]. The latter **contributes** less ESR signal due to interaction with neighboring cupric ions [22]. The **decrease** in Cu dispersion for catalysts with Cu/Al ≤ 0.051 can be attributed to the **formation** of interacting copper surface phase or copper oxide clusters.

For Cuy catalysts with Cu/Al atomic ratio ≥ 0.077 , the increase in XPS determined Copper oxide particle size with increasing Cu loading is consistent with the appearance of X-ray diffraction lines characteristic of CuO. These results are similar to previous work [21,26] which indicated that at a critical metal loading, the support becomes saturated With copper surface phase and further addition of the metal results in formation of CuO rystallites. The difference in CuO particle sizes determined using XPS and XRD may be attributed to the limitations of X-ray diffraction. It is well known that XRD determined

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particle sizes are skewed to large values since XRD does not detect highly dispersed species. For the Cu rich catalysts, a significant fraction of the copper is present as a surface phase or small CuO particles (d < 3.0 nm) that are detected by XPS, but not XRD. Thus, smaller average particle sizes are expected from XPS calculations.

Effect of Catalyst Structure on CO Oxidation Activity. The significant increase in CO oxidation TON as a function of Cu content observed for the Cuy catalysts suggests that CuO is the active phase for CO oxidation. In addition, when one considers that the crystalline CuO is poorly dispersed compared to the copper surface phase, it is clear that CuO is significantly more reactive than the copper surface phase. The increase in CO oxidation activity with increasing Cu loading observed in this study is not consistent with previous studies of CO oxidation over alumina supported copper oxide catalysts. The optimum copper contents have been reported as approximately 5 wt.% Cu/95 m²/g γ -Al₂O₃ [10] and 7 wt.% Cu on 200 m²/g γ -Al₂O₃ [33].

For the CO oxidation over alumina supported copper oxide catalysts, it is generally considered that CO oxidation involves redox phenomena on the surface of copper oxide. Jernigan and Somorjai [46] have recently proposed that CO oxidation proceeds by a redox mechanism involving CuO and Cu₂O and that the reduction of CuO by CO is the rate determining step. Since the oxidation reaction may require adsorption of CO at oxygen vacancies, the availability of oxygen vacancies is important for copper oxide based CO oxidation catalysts [11]. On the basis of CO TPR results, Severino et al. [10] have reported that the CuO crystalline phase is reduced at a lower temperature than the copper surface phase. Therefore, the high CO oxidation activity of the CuO phase can be attributed to more facile generation of oxygen vacancies during the CO oxidation reaction compared to the copper surface phase.

Effect of Catalyst Structure on CH₄ Oxidation Activity. The decrease in CH₄ oxidation activity with increasing Cu loading has been reported in previous studies [35,36]. Tsikoza et al. [35] suggested that CH₄ oxidation occurred primarily on the copper surface phase. In addition, Garbowski and Primet [28] have proposed that octahedrally coordinated surface copper ions are accessible to reactants involved in catalytic combustion reactions. Marion et al. [36] have reported that CH₄ oxidation activity for CuO/Al₂O₃ catalysts is proportional to the number of surface copper species and that the number of active centers decreased with increasing copper loading due to the decrease in Cu dispersion. In this study, the decrease in CH_4 oxidation activity for Cuy catalysts cannot be attributed to a change in Cu dispersion, since the turn over number was obtained by normalization with Cu dispersion. Instead, we propose that the isolated Cu^{2+} species are more reactive for CH_4 oxidation than the interacting copper surface species. For the high loading catalysts (Cu/Al \ge 0.077), the CH₄ oxidation activity is independent of Cu content, which can be ascribed to the formation of poorly dispersed CuO crystallites.

The mechanism of CH_4 oxidation differs in some respects from CO oxidation. First, the rate determining step of CH_4 oxidation involves C-H bond breakage [47]. Second, oxidation of CH_4 produces water which may poison catalysts [11]. Therefore CH_4 oxidation requires a higher reaction temperature, and thus the influence of oxygen vacancies will be less important due to high mobility of lattice oxygen [13]. Liu and Flytzani-Stephanopoulos [48] have proposed that acidic and basic sites on the catalyst surface play an important role for C-H bond breakage and formation of intermediate species. Isolated copper species may provide acidic/basic sites with more suitable strength and geometry for CH₄ oxidation than interacting copper species or crystalline CuO.

CH₄ TPR studies have been performed with CuO/Al₂O₃ catalysts. Kartheuser et al. [49] reported a broad, featureless peak in the range of 500-700 °C for a 5 wt.% CuO/325m²/g Al₂O₃ catalyst. They assigned this feature to the reduction of CuO or Cu-Al₂O₃. H₂ TPR results for Cu/Al₂O₃ catalysts showed that the reduction of copper surface phase occurs at a lower temperature than for CuO [37,50]. These H₂ TPR results are useful for understanding the high CH₄ oxidation activity of isolated copper species since both H₂ and CH₄ utilize hydrogen to reduce copper species and produce water.

4.6. Conclusions

The combined use of several techniques to investigate the effect of Cu loading on the structure and catalytic activity of Cu/Al₂O₃ catalysts for CO and CH₄ oxidation leads to the following conclusions.

1. For low Cu loadings (Cu/Al ≤ 0.051), copper exists as a dispersed copper surface phase. ESR results indicate that the fraction of interacting Cu phase increases with increasing Cu content. For Cu rich catalysts (Cu/Al ≥ 0.077), large CuO crystallites are formed.

2. The increase in CO oxidation activity observed with increasing Cu content can be attributed to an increase in concentration of crystalline CuO. The copper surface phase shows very low CO oxidation activity. This has been explained with the ease of CuO redox behavior compared to copper surface phase during the CO oxidation reaction.

3. The CH₄ oxidation activity decreases with increasing Cu loading. We propose that the isolated copper surface phase is more active for CH₄ oxidation than the interacting copper surface phase or crystalline CuO. For higher Cu loadings, the CH₄ oxidation activity is independent of Cu loading, which can be attributed to the formation of poorly dispersed CuO crystallites.

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Chapter 5

Characterization and CH₄ Oxidation Activity of Cr/Al₂O₃ Catalysts

5.1. Abstract

X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) have been used to characterize a series of Cr/Al₂O₃ catalysts (designated "Cry", y = Cr/Al atomic ratio). The information obtained from surface and bulk characterization has been correlated with CH₄ oxidation activity of the Cry catalysts. For catalysts with a Cr/Al atomic ratio y = 0.013, XPS results indicated that most of the Cr was present as a highly dispersed Cr⁶⁺ surface phase. Catalysts with intermediate Cr loadings ($y = 0.027 \sim 0.080$) showed no XRD peak characteristic of chromium oxide. However, XPS data indicated that the Cr dispersion decreased and the concentration of Cr³⁺ species increased with increasing Cr content. For catalysts with high Cr loadings (Cr/Al atomic ratio ≥ 0.107), large Cr₂O₃ crystallites were detected by XRD. The specific activity for CH₄ oxidation increase with increasing Cr content up to Cr/Al = 0.107. This has been attributed to an increase in the amount of Cr(III)-Cr(VI) cluster present in the catalysts. A decrease in CH₄ oxidation activity observed for a Cr rich catalyst (Cr/Al = 0.13) has been ascribed to the formation of poorly dispersed Cr₂O₃.

5.2. Introduction

Alumina supported chromium oxides have been studied extensively due to their potential application in emission control catalysis [1-3]. Desirable chemical and physical properties, such as low temperature efficiency for hydrocarbon [4-6] and chlorinated hydrocarbon oxidation [7-10], low selectivity for Cl₂ formation [8,11], high resistance to HCl poisoning [12] during chlorinated hydrocarbon oxidation, NO reduction with CO [13] and NH₃ [14], high thermal stability [6,15] and mechanical durability, [12] make Cr/Al₂O₃ catalysts suitable candidates for automotive emission control and industrial waste treatment. Chromium oxide is also an effective promoter for copper oxide catalysts used for CO and hydrocarbon oxidation and NO reduction [13,16,17].

The surface structure of alumina supported chromium oxide catalyst depends on the metal loading, calcination temperature and hydration/dehydration conditions [18-26]. For low chromium loadings ($\leq 10 \text{ wt.}\% \text{ Cr}_2\text{O}_3/\text{Al}_2\text{O}_3 200 \text{ m}^2/\text{g}$), most of the chromium is present as a highly dispersed Cr(VI) surface species. XPS studies indicate that the proportion of Cr(VI) on the alumina support decreases with increasing Cr content [18,19,21] or with increasing calcination temperature [21,27]. This has been attributed to the formation of Cr(III) species on the support surface [19,21,27]. Ellison and coworkers [28-32] studied Cr/Al₂O₃ catalysts using magnetic susceptibility, DRS, SIMS and ESR techniques. They proposed that a mixed oxidation state cluster ($-\text{Cr}^{6+}-\text{O}^2-\text{Cr}^{3+}-\text{O}^2-\text{Cr}^{6+}-;$ γ -phase) forms on the alumina support even at 1 wt.% Cr on 157 m²/g Al₂O₃. Wachs and coworkers [22,33] reported the monolayer coverage of chromium oxide (12 wt.% CrO_3/Al_2O_3 180 m²/g) based on Raman, XRD, and FTIR data. This is in good agreement with the theoretical monolayer coverage calculated from the cross section of $K_2Cr_2O_7$ [34] and ISS results [35]. For high chromium loadings (> 10 wt.% Cr_2O_3/Al_2O_3 200 m²/g), crystalline Cr_2O_3 is observed using Raman spectroscopy and X-ray diffraction. Bulk Cr(III)-Al₂O₃ forms after high temperature calcination (\geq 800 °C) of the Cr/Al₂O₃ containing crystalline Cr_2O_3 [22].

Despite the importance of Cr/Al_2O_3 catalysts in emission control applications, the study of CH₄ oxidation over Cr/Al_2O_3 catalysts has been relatively limited [36,37]. Little effort has been devoted to investigating systematically the relationship between the surface structure and the CH₄ oxidation activity of Cr/Al_2O_3 catalysts. Anderson et al. [36] have studied CH₄ oxidation over various alumina supported transition metal oxide catalysts and reported that chromium oxide shows the highest methane oxidation activity. Kuznetsova et al. [37] have reported that CH₄ oxidation activity increases and levels off with increasing Cr content. They proposed that Cr(VI) is the main active component for the CH₄ oxidation reaction.

The present work is part of a broad study to investigate structure-reactivity correlation for transition metal oxide based emission control catalysts. In this paper, Xray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) have been used to determine the effect of Cr loading on the chemical state and dispersion of chromium oxide Phases supported on γ-alumina. The information derived from these techniques is correlated with CH_4 oxidation activity to develop a more complete understanding of Cr/Al_2O_3 catalysts.

5.3. Experimental

Catalyst Preparation. The Cr-modified alumina carriers were prepared by pore volume impregnation of γ -alumina (Cyanamid, surface area = 203 m²/g, pore volume = 0.6 mL/g) using solutions of chromium (III) nitrate (Mallinckrodt, Analytical Reagent). The alumina was finely ground (<230 mesh) and calcined in air at 500 °C for 24 h prior to impregnation. The impregnated samples were dried at 120 °C for 24 h and calcined at 500 °C for 16 h. The chromium content of the Cr/Al₂O₃ series was varied from a Cr/Al atomic ratio of 0 to 0.134 (0 to 20 wt.% Cr₂O₃). Cr/Al₂O₃ catalysts will be designated by "Cry", where *y* is the Cr/Al atomic ratio (x 10²) of the catalysts. The catalyst colors change with increasing chromium content from pale yellow (Cr1.3), to yellow (Cr2.7), to dark yellow (Cr5.4), to brown (Cr8.0), to dark brown (Cr11 and Cr13).

Standard Materials. Cr_2O_3 was prepared by calcining chromium (III) nitrate at 500 °C for 16 h in air. CrO_3 (99.9 %) was obtained from Aldrich Inc. XRD patterns of the standard compounds matched the appropriate Powder Diffraction File [38].

BET Surface Area. Surface area measurements were performed using a QuantaChrome Quantasorb Jr. Sorption System. Approximately 0.1 grams of catalyst were outgassed in a N₂/He mixture (5% N₂) at 350 °C for 1 h prior to adsorption measurements. The measurements were made using relative pressures of N₂ to He of 0.05, 0.08, and 0.15 (N₂ surface area = 0.162 nm^2) at 77 K. Increasing the chromium content of the catalysts decreases the BET surface area by a maximum of 10%.

X-Ray Diffraction. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer employing Cu K_a radiation ($\lambda = 1.5418$ Å). The X-ray was operated at 45 kV and 100 mA. Diffraction patterns were obtained using a scanning rate of 0.5 deg/min (in 2 θ) with divergence slit and scatter slit widths of 1°. Samples were run as powders packed into a glass sample holder having a 20 x 16 x 0.5-mm cavity.

The mean crystallite sizes (\overline{d}) of the Cr₂O₃ particles were determined from XRD line broadening measurements using the Scherrer equation [39]:

$$\overline{d} = K\lambda / \beta \cos \theta \tag{1}$$

where λ is the X-ray wavelength, K is the particle shape factor, taken as 0.9, and β is the full width at half maximum (fwhm), in radians, of the Cr₂O₃<104> line.

Quantitative X-ray diffraction data were obtained by comparing $Cr_2O_3 < 104 > /Al_2O_3 < 400 >$ intensity ratios measured for catalyst samples with intensity ratios measured for physical mixtures of pure Cr_2O_3 , and γ -Al_2O_3. This method assumed **that chromium addition did not disrupt the** γ -Al_2O_3 spinel and subsequently affect the **imtensity of the** Al_2O_3 < 400 > line. The error in this method was estimated to be $\pm 20\%$.

XPS Analysis. XPS data were obtained using a Perkin-Elmer Surface Science **instrument equipped with a magnesium anode (1253.6 eV) operated at 300 W (15 kV, 20 mA) and a 10-360 hemispherical analyzer operated with a pass energy of 50 eV.** The **instrument typically operates at pressures near 1 x 10^{-8} torr in the analysis chamber.**

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Spectra were collected using a PC137 board interfaced to a Zeos 386SX computer. Samples were analyzed as powders dusted onto double-sided sticky tape or spray coated onto a quartz slide using a methanol suspension of the catalyst. Binding energies for the catalyst samples were referenced to the Al 2p peak (74.5 eV). The binding energies for standard compounds that did not contain Al were referenced to the C 1s line (284.6 eV) of the carbon overlayer. XPS binding energies were measured with a precision of \pm 0.2 eV, or better.

Reduction of chromium species [18,27,40] during XPS experiments has been reported and attributed to several factors such as X-ray flux, X-ray dose, temperature, and pressure. In order to minimize the effect of photoreduction on the results, all samples were analyzed using the same distance between X-ray source and sample (\sim 3/4 inch) and minimum data acquisition time (< 20 min.). No significant photoreduction was observed using these experimental conditions.

The oxidation state distribution of chromium was determined by non-linear leastsquares curve fitting (NLLSCF) using the Cr2p_{3/2} envelope [41]. Chromium peak positions were allowed to float slightly (± 0.1 eV) in order to fit the Cr2p_{3/2} envelope obtained for each sample. The full width at half maximum (fwhm) of Cr(III) was fixed at **3**.3 eV (determined using Cr₂O₃ as a reference compound). Since the fwhm of Cr(VI) measured for Cry catalysts did not agree with the value obtained for the CrO₃ standard **compound** (2.1 eV) and increased with decreasing Cr content, the fwhm of Cr(VI) was **allowed** to float near 3.0 eV (± 0.3 eV). The fwhm of standard compounds and Cry **Cata**lysts agree well with the values reported [42]. Scierka et al. [42] have examined the

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Cr2p envelope of Cr/Al₂O₃ catalysts with principal component analysis and target testing. The authors concluded that only Cr^{6+} and Cr^{3+} components are observed on the Cr/Al₂O₃ catalyst.

Quantitative XPS Analysis. It has been shown by Defosse et al. [43] that one may calculate the theoretical intensity ratio I_p^o/I_s^o expected for a supported phase (p) atomically dispersed on a carrier (s). An extension of the Defosse model proposed by Kerkhof and Moulijn [44] has been used in the present investigation. The photoelectron cross sections and the mean escape depths of the photoelectrons used in these calculations were taken from Scofield [45] and Penn [46], respectively. For a phase (p) present as discrete particles, the experimental intensity ratio I_p/I_s is given by the following expression:

$$I_{p}/I_{s} = I_{p}^{o}/I_{s}^{o} \left[1 - \exp\left(-d/\lambda_{p}\right)\right] / d/\lambda_{p}$$
(2)

where I_p^o/I_s^o is the theoretical monolayer intensity ratio, d is the length of the edge of the cubic crystallites of the deposited phase and λ_p is the mean escape depth of the **photoelectrons** in the deposited phase. The Cr species particle sizes were determined by **solving** the equation for d. The relative Cr dispersion to the monolayer was estimated **from** the ratio of I_p/I_s to I_p^o/I_s^o .

 CH_4 Oxidation Activity. Measurement of CH₄ oxidation activity was performed in **a** flow microreactor. Approximately 0.1 g of catalyst were supported on a glass frit (70 - **100** µm) and the temperature was measured with a K-type thermocouple located just **above** the catalyst bed. The reactor was heated by a tube furnace (Lindberg) with

temperature being controlled within 1°C by an Omega CN 1200 temperature controller. Reactant gas flow rates were held constant with Brooks 5850 mass flow controllers. Product gases were analyzed with a Varian 920 gas chromatograph equipped with a TCD and interfaced to a Hewlett-Packard 3394A integrator. Reaction products were separated on a 6 ft 60/80 mesh Carbosieve S-II column. Prior to the first activity measurement, the catalyst was pretreated with a mixture of 5% O2/He (99.5 % purity for O2, 99.995% purity for He, AGA Gas Co.) stream (143 cc/min) at 350 °C for 1 hr to remove any impurities adsorbed on the surface during catalyst preparation and storage. CH₄ oxidation reactions were performed with a constant flow rate (15 cm³/min) of 0.98 % CH₄/5.25 % O_{2} O₃ 77 % He gas mixture (AGA, purity > 99.99%) in the temperature range of 310-450 °C. Water produced during methane oxidation was frozen downstream from the reactor in a trap maintained < -40 °C with a mixture of ethanol and dry ice. All activity measurements were obtained under steady-state conditions at conversions less than 15 %. CO was observed as a partial oxidation product. The selectivity to CO_2 was in the range of 73-83 % over Cry catalysts at 10 % conversion. Turn over number (TON) was calculated with CH₄ oxidation rate at 390 °C normalized by surface chromium atoms determined from Cr content and dispersion.

5.4. Results and Discussion

Chemical State of Cr/Alumina Catalysts. XRD patterns obtained for Cry catalysts Cr/Al atomic ratios ≤ 0.080 showed only lines characteristic of the alumina carrier (Figure 5.1). For higher Cr loadings (Cr/Al atomic ratios ≥ 0.107), peaks characteristic of Cr₂O₃ were observed. The intensities of the Cr₂O₃ XRD peaks increase with increasing Cr content. Quantitative XRD measurements (Table 5.1) show that the amount of crystalline Cr₂O₃ increases from 0.9 to 5.5 wt.% as the Cr/Al atomic ratio increases from 0.107 to 0.134 (16 to 20 wt.% Cr₂O₃). Previous researchers have suggested that the support becomes saturated with surface chromium oxide at a critical metal loading and further Cr addition leads to the formation of crystalline Cr₂O₃ [22,47]. XRD results for the Cry catalysts indicate that the critical chromium loading is approximately 15 wt.% Cr₂O₃. Zaki et al. [47] have reported that crystalline Cr₂O₃ forms at 10.2 wt.% Cr₂O₃ on 135 m²/g Al₂O₃ support. This corresponds to 15.3 wt.% Cr₂O₃ after normalization for the surface area of alumina used in our study.

Figure 5.2 shows the Cr 2p XPS spectra obtained for the Cry catalysts. The average Cr 2p_{3/2} binding energies measured for the catalysts (579.7 ± 0.1 eV) are close to the value determined for CrO₃ (579.4 eV) and higher than the values obtained for Cr₂O₃ (576.4 eV). The Cr 2p_{3/2} spectra also contain a shoulder at lower binding energy (577.0 ± 0.2 eV) which is close to the value measured for Cr₂O₃. The intensity of the shoulder increases with increasing Cr loading. The binding energies measured for the standard compounds and catalysts agree well with values reported previously [18,21,27,35,48].
Comparison of binding energies measured for Cry catalysts and standard compounds indicates that the major peak and shoulder can be assigned to Cr(VI) and Cr(III), respectively. This is consistent with previous XPS studies of Cr/Al₂O₃ catalysts [18-21]
The showed that Cr(VI) species was present predominantly at low Cr concentration (< 5
** of Cr₂O₃ on 200 m²/g Al₂O₃) and the concentration of Cr(III) species increased with



Figure 5.1. XRD patterns measured for (a) Al₂O₃, (b) Cr11, and (c) Cr13.

	Crystalline Phase (wt%)		
Catalysts	As prepared	Measured	
Cr 1.3	2	_b	
Cr 2.7	4	_ ^b	
Cr 5.4	8	_ ^b	
Cr 8 .0	12	_ ^b	
Cr 11	16	0.9	
Cr 13	20	5.5	

Table 5.1.Concentration of Crystalline^a Phases in Cry Catalysts
Calculated from Quantitative XRD Data.

a - Valid for crystalline phases with particle sizes > 3.0 nm.

b - No Cr₂O₃ peaks detected for these catalysts.

increasing Cr content. The variation of the Cr $2p_{32}$ /Al 2p XPS intensity ratio of Cr(VI) and Cr(III) species for the Cry catalysts determined using non-linear least-squares curve fitting are shown in Table 5.2. The Cr(VI)/Al intensity ratio increases with increasing Cr/Al atomic ratio up to 0.054. For higher Cr loadings, the Cr(VI)/Al intensity ratios measured for the catalysts are independent of Cr content. This indicates that the alumina support becomes saturated with Cr(VI) species at the catalyst with Cr/Al atomic ratio = 0.054 (8 wt.% Cr₂O₃) and further addition of chromium only leads to the formation of Cr(III) species. Wachs and coworkers [22,33] have used the absence of Raman and XRD peaks of Cr₂O₃, the suppression of FTIR peaks of OH, and CO₂ chemisorption to show that monolayer coverage was reached at 12 wt.% CrO₃ (for 180 m²/g Al₂O₃). This **Corresponds** to 10 wt.% Cr₂O₃ after normalization for chromium oxide molecular formula **and** surface area of alumina used in our study. The discrepancy between the XRD and **XPS** data for saturation point (15 wt.% and 8 wt.% Cr₂O₃/Al₂O₃, respectively) is due to **the** different detection limits (selectivity) of the techniques. The saturation point



Cr 2p XPS spectra obtained for (a) Cr1.3, (b) Cr2.7, (c) Cr5.4, (d) Cr8.0, (e) Cr11, and (f) Cr13 catalysts.

	Intensit	ty Ratio
Catalysts	Cr(VI)/Al	Cr(III)/Al
Cr 1.3	0.21	0.05
Cr 2.7	0.31	0.13
Cr 5.4	0.57	0.25
Cr 8 .0	0.54	0.45
Cr 11	0.52	0.64
Cr 13	0.51	0.75

Table 5.2. Cr 2p_{3/2}/Al 2p XPS Intensity Ratios of Cr(VI) and Cr(III) Species in Cry Catalysts Determined Using Non-Linear Least-Squares Curve Fitting (NLLSCF).

CVI) species are used for the determination derived from XPS. The Cr(III) species are Served from the Cr1.3 catalyst and the Cr(III)/Al XPS intensity ratio increases with Creasing Cr content (Table 5.2). The Cr(III) species on the low Cr content catalysts Celow monolayer coverage) has been detected by ESR [28-32] and XPS [18-20,42] Chniques. The presence of Cr(III) species has been attributed to cluster formation [30] Creatination induced reduction [21]. The relative distributions of Cr(VI) and Cr(III) Species for the low Cr loading catalysts (e.g. 19 % Cr(III) for Cr1.3) are similar to the Catalysts (Cr/Al₂O₃ (170 m²/g) catalyst which corresponds to 4.4 wt.% Cr₂O₃ for Create alysts (Cr11 and Cr13) can be attributed to the formation of crystalline Cr₂O₃. Dispersion of Cr/Alumina Catalysts. Figure 5.3 shows the variation of the Cr 2 2 2 2 2 12p intensity ratio measured for the Cry catalysts as a function of the Cr/Al atomic ratio. The theoretical line calculated for monolayer dispersion [44] is shown for comparison. The Cr/Al intensity ratio measured for the Cr1.3 catalyst is identical, within measured for the Cr1.3 catalyst is identical, within comparison. The Cr/Al intensity ratio measured for the Cr1.3 catalyst is identical, within comparison, to the value predicted for monolayer dispersion. For higher Cr loadings, the Cr/Al intensity ratios measured for the catalysts are lower than the monolayer values. The increasing deviation of the Cr/Al intensity ratio from the monolayer line with increasing Cr loading indicates that the Cr dispersion decreases the formation of chromium oxide cluster or crystalline on the alumina support as a method of Cr content.

Variation in the particle size of the chromium phase determined from Cr/Al XPS Tensity ratios using Eq. (2) is given as a function of the Cr loading in Table 5.3. The mean particle size of the chromium phase calculated from XPS intensity ratios increases from 0.5 to 1.9 nm with increasing Cr content. Particle sizes determined from XRD line broadening calculations using Eq. (1) are also shown in Table 5.3. For catalysts with Cr/Al atomic ratios ≥ 0.107 , XRD line broadening calculations show that the Cr₂O₃ particle sizes are significantly larger than the values determined using XPS. The difference in Cr₂O₃ particle sizes determined using XPS and XRD may be attributed to the limitations Of X-ray diffraction. It is well known that XRD determined particle sizes are skewed to large values since XRD does not detect highly dispersed species. For the Cr rich catalysts, a significant fraction of the chromium is present as a surface phase or small Cr₂O₃ particles



Trigure 5.3. Cr 2p/Al 2p XPS intensity ratios measured for Cry catalysts (**•**) plotted versus Cr/Al atomic ratio. Cr 2p/Al 2p intensity ratios calculated for monolayer dispersion (line).

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Particle size (nm)			
Catalysts	XRD	XPS	Dispersion ^c (%)
Cr 1.3	_ ^a	-6	100
Cr 2.7	_*	0.5	75.8
Cr 5.4	- a	0.8	67.6
Cr 8 .0	_ ^a	1.2	55.7
Cr 11	46	1.5	50.8
Cr 13	29	1.9	42.4

Table 5.3.Particle Size and Dispersion of Chromium PhasesDeterminedfromXRDLineBroadeningCalculations and Cr/Al XPS Intensity Ratios.

a - No Cr_2O_3 peaks detected for these catalysts.

b - Value corresponds to monolayer dispersion.

c - Calculated from XPS data.

Cd < 3.0 nm) that are detected by XPS but not XRD. Thus, smaller average chromium
 Side particle sizes are expected from XPS calculations.

Based on the XRD and XPS results presented above, the effect of chromium adding on Cry catalyst structure can be summarized as follows: (1) for low Cr loadings, for the Cr is present as a highly dispersed Cr(VI) surface phase, (2) the fraction of r(III) species present in the catalysts increases and the Cr dispersion decreases with creasing Cr content, and (3) Cr rich catalysts contain large Cr₂O₃ particles.

Effect of Catalyst Structure on CH_4 Oxidation Activity. Table 5.4 shows the Specific turnover number (TON) for CH_4 oxidation over Cry catalysts calculated at 390 °C Sing XPS estimates of the Cr dispersion. The TON increases approximately by a factor of 3 as the Cr/Al atomic ratio increases from 0.013 to 0.11. Further addition of Cr Creases the TON for CH_4 oxidation. The activation energies for CH_4 oxidation (Table

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5 _ **4**) calculated for the Cry catalysts are similar within experimental error $(20.2 \pm 0.9 \text{ K})$.

The variation in TON for CH₄ oxidation as a function of Cr loading can be \sim **I** ained in terms of the surface structure of the Cry catalysts. The increase in TON with imcreasing Cr/Al ratio over the range 0.013 to 0.107 parallels a significant increase in the **T**(**II**) content of the catalysts (Table 5.2). The increase in TON as a function of Cr **1 a d**ing up to Cr11 catalyst can be attributed to an increase in the formation of Cr(III)- \sim **T**(**V**I) clusters that may be more active for CH₄ oxidation than Cr(VI) species. The Carlanced activity of an alumina supported Cr(III)-Cr(VI) species has been reported for Several different reactions [28-32,47-52]. Ellison and coworkers [28,31,32] have **P** $\boldsymbol{\tau}$ oposed that the mixed oxidation state cluster (γ -phase) has high catalytic activity for Teactions that require both oxidation and reduction process (Zener mechanism). In Addition, Zaki and coworkers [47,49,50] have reported that the y-phase was the active site H_2O_2 and propanol decomposition over chromium catalysts. For the Cr13 catalyst, the Crease in TON relative to the Cr11 catalyst may be correlated to an increase in the arrount of large Cr₂O₃ particles present in the Cr rich catalyst. Large Cr₂O₃ particles will Frace fewer Cr(III)-Cr(VI) interfacial interactions compared to small Cr_2O_3 particles. **This** yama et al. [51,52] have reported that the γ -phase was more active than bulk Cr₂O₃ for reduction with NH₃. They proposed that the metal - surface oxygen bond strength of The γ -phase was weaker than that of bulk Cr_2O_3 .

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Catalysts	TON $(s^{-1}x10^{4})$	Activation Energy
Cr 1.3	2.8	21.7
Cr 2.7	3.4	20.4
Cr 5.4	4.5	20.3
Cr 8 .0	5.7	19.8
Cr 11	7.3	20.2
Cr 13	5.6	18.8

Table 5.4. Turn Over Numbers^a and Activation Energies^b of Cry Catalysts for CH₄ Oxidation.

a - Calculated at 390 °C using exposed Cr species determined from XPS.

b - Estimated from Arrhenius plots.

5.5. Conclusions

The combined use of several techniques to investigate the effect of Cr addition on the structure and CH_4 oxidation activity of Cry catalysts leads to the following conclusions.

1. XPS data indicate that most of the Cr is present as a highly dispersed Cr(VI) Surface phase in Cr1.3 catalyst. The fraction of Cr(III) increases and the Cr dispersion Creases with increasing Cr loading. Cr-rich catalysts (Cr11 and Cr13) contain large Systallites of Cr_2O_3 .

2. The TON for CH_4 oxidation increases by a factor of 3 with increasing **hromium** loading up to the Cr11 catalyst. This has been attributed to the formation of a **r(III)-Cr(VI)** cluster. Further addition of Cr decreases the TON due to the formation of **Poorly** dispersed Cr_2O_3 crystallites.

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Chapter 6

Characterization and CO Oxidation Activity of Cu/Cr/Al₂O₃ Catalysts

6.1. Abstract

X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) have been used to characterize a series of Cu/Cr/Al₂O₃ catalysts. The catalysts were prepared by stepwise incipient wetness impregnation of chromium first, followed by copper. The copper loading was held constant at 8 wt.% CuO and chromium loadings were varied from Cr/Al atomic ratios from 0 to 0.0134 (0 to 20 wt.% Cr₂O₃). The information obtained from surface and bulk characterization has been correlated with CO oxidation activity of the Cu/Cr/Al₂O₃ catalysts. The copper addition decreased the dispersion of chromium phase by reacting selectively with a dispersed Cr^{3+} species to form large crystalline CuCr₂O₄. The Cu dispersion also decreased with increasing Cr loading. For low Cr loading catalysts (Cr/Al ≤ 0.027), CO oxidation activity increased with the addition of Cr due to the formation of crystalline CuO on the chromium modified alumina. This has been attributed to the prevention of Cu ion diffusion to alumina lattice vacancies by highly dispersed chromium species. The Cu/Cr/Al₂O₃ catalyst of Cr/Al = 0.054 showed the highest CO oxidation activity due to the formation of an active CuCr₂O₄ phase. For further addition of Cr (Cr/Al ≥ 0.080), the catalytic activity for CO oxidation decreased.
6.2. Introduction

The combination of copper and chromium oxide was recognized as a promising active component for emission control reactions in the early years of pollution control catalysis research [1-5]. The Cu-Cr catalyst system has been studied extensively for various reactions, including CO oxidation [6-21], hydrocarbon oxidation [6-10,22-23], NO reduction [19-20,24], alcohol and aldehyde oxidation [25-26], and sulfurnated [27] and chlorinated [28] hydrocarbon oxidation. Shelef et al. [4] and Kapteijn et al. [20] have performed a screening study of transition metal oxide catalysts for CO oxidation and NO reduction. They have reported that Cu-Cr catalysts showed consistently higher catalytic activity than single oxide catalysts based on Cu, Ni, Co, Fe, Mn, Cr, or V. Barnes [6] studied automotive pollution control catalysts for exhaust treatment such as CO and hydrocarbon oxidations. He reported that the alumina supported 8 wt.% Cu-7 wt.% Cr catalyst showed similar activity to 0.3 wt.% Pt catalyst. In addition, Stegenga et al. [29] have found that monolith supported 10 wt.% Cu-Cr/Al₂O₃ catalyst showed a three-way catalytic behavior (CO and hydrocarbon oxidation, and NO reduction, simultaneously) comparable to noble metal catalysts operated under the same conditions.

In the copper chromite catalyst system, copper oxide has been proposed as an active component for CO oxidation reaction, while chromium oxide has been considered

as a promoter [13,19,23,30]. The roles of Cr promoter to the Cu species are believed to limit catalyst reduction [12-14,24,31], prevent catalyst poisoning [10,12,15], inhibit bulk copper aluminate formation [30], improve thermal stability [10], and increase catalyst dispersion [17,30]. Furthermore the mixed oxide catalyst shows greater activity and stability than the single oxide catalysts [32,33]. The synergistic effect of Cu-Cr catalysts has been attributed to the electronic interaction between copper and chromium species [13,17,23].

Despite a considerable amount of effort devoted to the study of Cu-Cr catalyst, the understanding of Cu-Cr catalyst system is still not clear. Stegenga et al. [29] reported that the optimum metal composition of Cu-Cr/Al₂O₃ catalyst was Cu/Cr = 2 for CO oxidation. However, Severino et al. [12] found that Cu/Cr = 1 was a optimal metal composition of alumina supported catalyst for CO oxidation. Also, uncertainty has arisen with regard to the pretreatment for the most efficient catalyst. Severino et al. [12] reported that catalyst prereduction enhanced catalytic activity efficiently for CO oxidation. However, Chien et al. [23] showed that oxidative pretreatment of Cu-Cr catalyst was more beneficial than reductive pretreatment for CO oxidation.

Much of the previous research on the Cu-Cr catalysts have focused on the understanding of catalytic properties such as activity or stability. Little effort has been devoted to the relationship between surface structure of Cu/Cr/Al₂O₃ and its catalytic activity. The present work is a part of a broad study to investigate the effect of base metal oxide promoters on the structure and reactivity of copper oxide based emission control catalysts. In this paper, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction

(XRD) were used to determine the effect of Cr loading on the chemical state and dispersion of chromium and copper oxide phases supported on γ -alumina. The information derived from these techniques has been correlated with CO oxidation activity to develop a more complete understanding of the Cu/Cr/Al₂O₃ catalyst.

6.3. Experimental

Standard Materials. CrO_3 (99.9 %) was obtained from Aldrich Chemical Company, Inc. CuO and Cr_2O_3 were prepared by calcining metal nitrates in air at 500 °C for 16 h. $CuCr_2O_4$ and $CuAl_2O_4$ were prepared by calcining stoichiometric mixtures of the respective nitrates in air at 1000 °C for 24 h. XRD patterns of the standard compounds matched with the appropriate Powder Diffraction File [34].

Catalyst Preparation. Catalysts were prepared by pore volume impregnation of γ alumina (Cyanamid, γ -Al₂O₃, surface area = 203 m²/g, pore volume = 0.6 mL/g). The alumina support was finely ground (< 230 mesh) and calcined in air at 500 °C for 24 h prior to impregnation. Catalysts were prepared using deionized water solutions of chromium(III) nitrate (Mallinckrodt, Analytical Reagent) and copper(II) nitrate (Columbus Chemical Industries Inc, ACS Grade). The impregnated catalysts were dried in air at 120 °C for 24 h and subsequently calcined in air at 500 °C for 16 h. Mixed metal oxide catalysts (Cu/Cr/Al₂O₃) were prepared by the step wise impregnation of chromium first, followed by Cu. Chromium impregnated alumina (Cr/Al₂O₃) was dried and calcined prior to the introduction of copper. Catalysts with added copper were dried and calcined again under the same conditions. The copper content was held constant at 8 wt.% (as CuO) of the alumina support. The chromium content was varied from an Cr/Al atomic ratio of 0 to 0.134 (0 to 20 wt.% Cr_2O_3). Catalyst samples will be designated by "Cry" and "CuCry", where y is the Cr/Al atomic ratio (x 10²).

BET Surface Area. Catalysts surface area were determined using a QuantaChrome Quantasorb Jr. Sorption System. Approximately 0.1 g of catalyst was outgassed in a N_2 /He mixture (5% N_2) at 350 °C for 1 h prior to adsorption measurement. The measurement was made using relative pressures of N_2 to He of 0.05, 0.08, and 0.15 (N_2 surface area = 0.162 nm²) at 77 K. The BET surface areas of catalyst samples decreased with increasing catalyst loading by a maximum of 20 %.

X-Ray Diffraction. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer employing Cu K α radiation ($\lambda = 1.5418$ Å). The diffractometor was operated at 45 kV and 100 mA. Diffraction patterns were obtained using a scan rate of 0.5 deg/min. with divergence slit and scatter slit widths of 1°. Samples were run as powders packed into a glass sample holder having a 20 x 16 x 0.5-mm cavity. The mean crystalline sizes (\overline{d}) of the CuO, Cr₂O₃, and CuCr₂O₄ particles were determined from XRD line broadening measurement using the Scherrer equation [35]:

$$d = K \lambda / \beta \cos \theta \tag{1}$$

where λ is the X-ray wavelength, K is the particle shape factor, taken as 0.9, and β is the

full width at half maximum (fwhm), in radians, of the CuO $<\overline{1}11>$, Cr₂O₃<104>, or CuCr₂O₄<311> lines. Quantitative X-ray diffraction data were obtained by comparing

CuO $<\overline{1}11>$, Cr₂O₃<104>, or CuCr₂O₄<311> vs Al₂O₃<400> intensity ratios measured for catalyst samples with intensity ratios measured for the physical mixtures of pure CuO, Cr₂O₃, or CuCr₂O₄ and γ -Al₂O₃. This method assumes that copper and chromium addition does not disrupt the γ -Al₂O₃ spinel and subsequently affect the intensity of the Al₂O₃<400> line. The error in this method was estimated to be ± 20 %.

XPS Analysis. XPS data were obtained using a Perkin-Elmer Surface Science instrument equipped with a magnesium anode (1253.6 eV) operated at 300 W (15 kV, 20 mA) and a 10-360 hemispherical analyzer operated with a pass energy of 50 eV. The instrument typically was operated at pressures near 1 x 10⁻⁸ torr in the analysis chamber. Spectra were collected using a PC137 board interfaced to a Zeos 386SX computer. Samples were analyzed as powders dusted onto double-sided sticky tape or spray coated onto a quartz slide using a methanol suspension of the catalyst. Binding energies for the catalyst samples and CuAl₂O₄ were referenced to the Al 2p peak (74.5 eV). The binding energies for standard compounds with no Al were referenced to the C 1s line (284.6 eV) of the carbon overlayer. XPS binding energies were measured with a precision of \pm 0.2 eV, or better.

Reduction of copper [36-38] and chromium [39-41] species during the XPS experiment has been reported and attributed to several factors such as X-ray flux, X-ray dose, temperature, and pressure. In order to minimize the effect of photoreduction on the

results, all samples were analyzed using the same X-ray flux, a constant distance between the X-ray source and the sample, and a minimum data acquisition time.

Quantitative XPS Analysis. It has been shown by Defosse et al. [42] that one may calculate the theoretical intensity ratio I^{o}_{p}/I^{o}_{s} expected for a supported phase (p) atomically dispersed on a carrier (s). An extension of the Defosse model proposed by Kerkhof and Moulijn [43] has been used in the present investigation. The photoelectron cross sections and the mean escape depths of the photoelectrons used in these calculations were taken from Scofield [44] and Penn [45], respectively. For a phase (p) present as discrete particles, the experimental intensity ratio I_p/I_s is given by the following expression:

$$I_{p}/I_{s} = I_{p}^{\circ}/I_{s}^{\circ} \left[1 - \exp\left(-d/\lambda_{p}\right)\right] / d/\lambda_{p}$$
(2)

where I_p^o/I_s^o is the theoretical monolayer intensity ratio, d is the length of the edge of the cubic crystallites of the deposited phase and λ_p is the mean escape depth of the photoelectrons in the deposited phase.

Curve Fitting. XPS data manipulation performed using 'GOOGLY' PC software [46]. The Cr $2p_{3/2}$ range was used to measure Cr binding energies and a relative oxidation state distribution by non-linear least-squares curve fitting (NLLSCF). The Cr peak positions were allowed to float slightly (± 0.1 eV) in order to fit into the Cr $2p_{3/2}$ envelope of each sample. The full width at half maximum (FWHM) of Cr(III) was fixed as 3.3 eV, a value that was determined from the line width for Cr₂O₃. The Cr(VI) FWHM of Cr/Al₂O₃ catalysts did not agree with the value for CrO₃ (2.1 eV). Also, the width

increased with decreasing Cr content. The FWHM of Cr(VI) was allowed to float from $3.0 \pm 0.3 \text{ eV}$. Those FWHM of standard compounds and Cr/Al₂O₃ catalysts are well agreed with the values reported by Scierka et al [41].

Catalytic Activity Measurement The measurement of CO oxidation activity was performed in a flow microreactor (1/2 inch glass tube). Approximately 0.03 g of catalyst was supported on a glass frit (70 - 100 μ m) and the temperature was measured with a Ktype thermocouple located just above the catalyst bed. The reactor was heated by a tube furnace (Lindberg) with temperature being controlled within 1 °C by an Omega CN 1200 temperature controller. Reactant gas flow rates were held constant with Brooks 5850 mass flow controllers. Product gases were analyzed with a Varian 920 gas chromatography equipped with a TCD and interfaced to a Hewlett-Packard 3394A integrator. Reaction products were separated on a 6 ft 60/80 mesh Carbosieve S-II column. Prior to the first activity measurement, the catalysts were pretreated with a mixture of 5% O₂/He (99.5 % purity for O₂, 99.995% purity for He, AGA Gas Co.) stream (143 cc/min) at 350 °C for 1 hr to remove any impurities adsorbed on the surface during catalyst preparation and storage. CO oxidation reactions were performed with a 80 cm^{3}/min flow of 4.8% CO/9.8% O₂/85.4% He gas mixture (AGA, purity > 99.99%). The reaction rate was calculated from the TCD sensitivity corrected CO and CO₂ chromatographic response of the reactor output. All activity measurements were obtained under steady-state conditions at conversions less than 15 %. The specific turn over number (TON) was calculated from the CO oxidation rate at 240 °C which was normalized with respect to Cu dispersion as estimated by XPS data. The activation energy was determined from an Arrhenius plot for CO oxidation.

6.4. Results and Discussion

Chemical Composition of Cu/Cr/Al₂O₃ Catalysts

Standard Compounds. The XPS Cu $2p_{3/2}$ binding energies and satellite/main peak intensity ratios for standard compounds are shown in Table 6.1. CuAl₂O₄ and CuCr₂O₄ have higher binding energies and satellite/main peak intensity ratios than the values obtained for CuO. Those binding energies and satellite/main peak intensity ratios of the standard compounds are consistent with previously reported values [38,47,48].

 Cu/Al_2O_3 Catalyst. The XPS Cu $2p_{3/2}$ binding energy measured for the CuCr0 catalyst is higher than the value obtained for CuAl_2O₄ and CuO, but closer to the value of CuAl_2O₄ (Table 6.1). Figure 6.1 shows the XRD patterns obtained for alumina support and CuCry catalysts. The XRD pattern of the CuCr0 catalyst shows only lines characteristic of alumina. The XPS and XRD results indicate the predominant presence of dispersed copper 'surface spinel' phase on the alumina support [38,48]. However, the satellite/main peak ratio measured for the CuCr0 catalyst is closer to the value of CuO than to that of CuAl_2O₄. This result conflicts with XRD data which indicates the absence of crystalline CuO for the CuCr0 catalyst. Strohmeier et al. [38] have explained this discrepancy that well dispersed or amorphous CuO was not necessarily present on the

Cr/Al Atomic Ratio (x10 ²)	B.E. of Cu 2p _{3/2}	shakeup/main peak ratio
0.0	935.4	0.42
1.3	935.3	0.48
2.7	935.5	0.56
5.4	935.5	0.62
8.0	935.5	0.63
10.7	935.5	0.69
13.4	935.5	0.72
CuO	933.9	0.45
CuAl ₂ O₄	935.0	0.71
CuCr ₂ O ₄	934.5	0.70

Table 6.1.XPS Cu 2p_{3/2} Binding Energies and Shakeup/Main
Peak Intensity Ratios Measured for CuCry Catalysts
and Standard Compounds.

catalyst, but the surface spinel copper species might be chemically different from both bulk CuO and CuAl₂O₄.

Cu/Cr/Al₂O₃ Catalysts. The average XPS Cu $2p_{3/2}$ binding energy measured for CuCry catalysts (935.5 ± 0.1 eV) is identical, within experimental error, to the value obtained for CuCr0 catalyst (Table 6.1). This indicates that the addition of chromium had little effect on the XPS Cu $2p_{3/2}$ binding energies measured for the catalysts.

Figure 6.2 shows the Cr 2p XPS spectra of CuCry catalysts. The Cr $2p_{3/2}$ binding energies of a main peak (580.0 ± 0.1 eV) and a shoulder (577.4 ± 0.1 eV) measured for the catalysts has been assigned to the Cr(VI) and Cr(III) species, respectively [49]. The relative distribution of Cr(VI) and Cr(III) oxidation states in CuCry catalysts indicates that Cr(III) species increase with increasing Cr content (Table 6.2). The XPS binding energies -----



Figure 6.1. XRD patterns measured for CuCry catalysts (● alumina, ■ CuO, ◊ cubic CuCr₂O₄, ∇ tetragonal CuCr₂O₄, ↔ Cr₂O₃). (a) alumina (b) CuCr0, (c) CuCr1.3, (d) CuCr2.7, (e) CuCr5.4, (f) CuCr8.0, (g) CuCr10.7, and (h) CuCr13.4.



Figure 6.2. Cr $2p_{3/2}$ XPS spectra measured for CuCry catalysts. (a) CuCr1.3, (b) CuCr2.7, (c) CuCr5.4, (d) CuCr8.0, (e) CuCr10.7, and (f) CuCr13.4.

and relative oxidation state distribution of Cr species for the CuCry catalysts are consistent with the results obtained for Cry catalysts within experimental error [49]. This indicates that the post-addition of Cu does not affect Cr oxidation states in CuCry catalysts.

Our previous study [49] indicated that the chromium oxide structure of Cry catalysts depended on the Cr content. Three levels of Cr loading will be discussed the structure of CuCry catalysts: low Cr loading (0.013 \leq Cr/Al atomic ratios \leq 0.027), intermediate Cr loading (0.054 \leq Cr/Al \leq 0.080) and high Cr loading (Cr/Al \geq 0.107).

For CuCry catalysts with low Cr loading, the XRD patterns show peaks characteristic of CuO (Figure 6.1). Table 6.3 shows the amount of crystalline CuO, tetragonal CuCr₂O₄ and Cr₂O₃ present in the CuCry catalysts as a function of Cr/Al atomic ratio. The amount of crystalline CuO increases from 0.4 to 1.9 wt.% as the Cr/Al atomic ratio increases from 0.013 to 0.027. The formation of CuO phase can be explained in terms of a decrease in interaction between copper species and alumina support [50]. A significant number of the lattice vacant sites normally accessible to the Cu²⁺ ions during catalyst preparation steps are blocked by pre-loaded chromium oxide species (well dispersed $Cr^{6^{-}}$ species). Thus, $Cu^{2^{+}}$ ions are not able to enter the alumina lattice to form the copper surface spinel phase. Upon calcination, these Cu^{2+} ions agglomerate to form large particles of CuO. The formation of a CuO phase on the Cr-modified alumina indicates that the copper species does not readily interact with the Cr⁶⁺ species to form $CuCr_2O_4$ phase. This is consistent with the result of the relative distribution of Cr(VI) and Cr(III) oxidation states in CuCry catalysts which were similar to the values of Cry catalysts [49]. For CuCry catalysts with intermediate Cr loading, the XRD patterns show

Table 6.2.Distribution of Cr Oxidation States Determined from
Cr 2p_{3/2} XPS Spectra of CuCry Catalysts Measured
by Non-Linear Least-Squares Curve Fitting
(NLLSCF).

Cr/Al Atomic Ratio	Relative conc	entration (%)
(x10 ²)	Cr(VI)	Cr(III)
1.3	79	21
2.7	77	23
5.4	73	27
8.0	57	43
10.7	54	46
13.4	47	53

Table 6.3.	Concentration	of	Crystalline ^a	Phases	in	CuCry
	Catalysts Calcu	late	d from Quant	itative X	RD	Data.

Cr/Al Atomic	Weight Percent of Crystalline Phase		
Ratio (x10 ²)	Cr_2O_3	CuO	CuCr ₂ O ₄
0.0	b	0.0	b
1.3	0.0	0.4	0.0
2.7	0.0	1.9	0.0
5.4	0.0	0.0	0.3
8.0	0.0	0.0	3.4
10.7	1.3	0.0	3.4
13.4	8.1	0.0	3.1

a - Valid for crystalline phases with particle sizes > 3.0 nm.

b - Catalyst does not contain chromium.

peaks characteristic of tetragonal CuCr₂O₄ (Figure 6.1). In addition, a peak observed at 35.9° in the diffraction pattern of the CuCr5.4 catalyst can be assigned to a cubic CuCr₂O₄ <311>. The crystalline tetragonal CuCr₂O₄ content of the catalysts increases from 0.3 to 3.4 wt.% as the Cr/Al atomic ratio increases from 0.054 to 0.080 (Table 6.3). For CuCr5.4 and CuCr8.0 catalysts, the XRD patterns indicate that CuCr₂O₄ is the major crystalline phase. This is consistent with the increase of the Cu $2p_{3/2}$ XPS satellite/main peak ratio up to 0.63 (Table 6.1).

For CuCry catalysts with high Cr loading, the peaks characteristic of crystalline Cr_2O_3 are observed in the XRD patterns (Figure 6.1). The crystalline Cr_2O_3 content of the catalysts increases from 1.3 to 8.1 wt.%, however, the crystalline $CuCr_2O_4$ content is independent of the Cr addition as the Cr/Al atomic ratio increases from 0.107 to 0.134 (Table 6.3). The Cu $2p_{3/2}$ XPS satellite/main peak intensity ratios for the high Cr loading catalysts (Table 6.1) are close to the value obtained for $CuCr_2O_4$. This result indicates that most of the Cu reacts with Cr species to form $CuCr_2O_4$ instead of interacting with the alumina support. The comparable Cr_2O_3 content obtained for the CuCry and the analogous Cry catalysts [49] suggests that little $CuCr_2O_4$ phase is formed by the interaction of Cu with large Cr_2O_3 crystallites. This is readily understood when one considers that large Cr_2O_3 crystallites have relatively less surface area available to react with Cu species than small Cr_2O_3 crystallites.

Dispersion of Cu/Cr/Al₂O₃ Catalysts.

Copper species. Figure 6.3 shows the variation of the Cu 2p_{3/2}/Al 2p XPS intensity ratios measured for the CuCry catalysts as a function of Cr/Al atomic ratio. The decrease in the XPS intensity ratios with increasing Cr content indicates a decrease of Cu species dispersion in CuCry catalysts as a function of Cr loading [43]. However, it should be noted relatively high Cu $2p_{3/2}$ /Al 2p XPS intensity ratio observed for CuCr5.4 catalysts. This is probably due to the formation of CuCr₂O₄ phase from well dispersed Cr oxide species on the alumina support. The variation in copper particle size as a function of Cr content determined from Cu/Al XPS intensity ratios and XRD line broadening is shown in Table 6.4 and 6.5, respectively. The particle size of Cu species in CuCr0 catalyst (1.0 nm) calculated from XPS data indicates that Cu is well dispersed over alumina carrier. This is consistent with XRD result which does not show any crystalline phase. The Cu phase particle sizes calculated from XPS data increase from 1.0 to 2.1 nm with increasing Cr loadings. This result agrees with XRD data that the formation of large CuO and CuCr₂O₄ crystallites is observed in the CuCry catalysts with increasing Cr content. CuO and $CuCr_2O_4$ particle sizes determined using XRD line broadening calculations are significantly larger than the particles sizes determined from XPS data. The difference in particle size determined from XPS and XRD results may be understood in terms of the detection limit of XRD. Since XRD detects large particles (> 3 nm) exclusively, the particle sizes calculated from XRD line broadening result have tendency to be large values.

Chromium species. Figure 6.4 shows the variation of the Cr 2p/Al 2p XPS intensity ratios measured for CuCry catalysts (open circles) as a function of Cr/Al atomic ratio. Cr 2p/Al 2p XPS intensity ratios obtained for the analogous Cry catalysts (solid



Figure 6.3. Cu $2p_{3/2}$ /Al 2p XPS intensity ratios of CuCry catalysts plotted versus Cr/Al atomic ratio. Monolayer dispersion value = 2.28.

Cr/Al Atomic	Particle Size (nm)	
Ratio (x10 ²)	Chromium	Copper
0.0	a	1.0
1.3	Ь	1.3
2.7	0.7	1.5
5.4	1.2	1.4
8.0	2.0	1.8
10.7	2.0	2.1
13.4	2.5	2.1

Table 6.4.Particle Sizes of Chromium and Copper SpeciesDetermined from XPS Intensity Ratios.

a - Catalyst does not contain chromium.

b - Catalyst dispersion is close to monolayer.

Table 6.5.	Particle Sizes	of CuO,	Cr_2O_3 ,	and CuC	Cr ₂ O ₄ Phases
	Determined	from	XRD	Line	Broadening
	Calculations.				

-				
	Cr/Al Atomic	<u>C</u>	Particle Size(nm)	
_	Ratio (x10 ⁻)	CuO	CF_2O_3	$CuCr_2O_4$
_	0.0	а	b	b
	1.3	17	a	а
	2.7	16	a	а
	5.4	а	a	31
	8 .0	а	a	29
	10.7	а	44	30
	13.4	a	33	28

a - No diffraction lines detected.

b - Catalyst does not contain chromium.



Figure 6.4. Cr 2p/Al 2p XPS intensity ratios of Cry (•) and CuCry(O) catalysts plotted versus Cr/Al atomic ratio. Cr 2p/Al 2p intensity ratios calculated for monolayer dispersion (line).

circles) [49] and the theoretical line calculated from the Kerkhof and Moulijn model [43] for monolayer dispersion are also shown for comparison. The Cr/Al intensity ratios measured for the CuCry catalysts with Cr/Al atomic ratio ≤ 0.027 are similar to the values measured for Cry catalysts. The absence of XRD peaks characteristic of discrete Cr phases and the similarity of the Cr/Al intensity ratios measured for the catalysts with the values calculated for monolayer dispersion indicate that Cr is highly dispersed over the alumina carrier. For the CuCry catalysts with Cr/Al atomic ratio ≥ 0.054 , the Cr/Al intensity ratios are lower than the values obtained for the analogous Cry catalysts. This indicates that Cu addition decreases the dispersion of the Cr species. This is consistent with XRD results which showed large crystalline CuCr₂O₄ and Cr₂O₃ phases for the catalysts with Cr/Al atomic ratio ≥ 0.054 . The variation in Cr phase particle size as a function of Cr loading determined from Cr/Al XPS intensity ratios and XRD line broadening is shown in Tables 6.4 and 6.5, respectively. Cr particle sizes calculated from XPS data generally increase with increasing Cr loading. As for the copper species, the Cr_2O_3 particle sizes determined for CuCry catalysts using XRD line broadening calculations are significantly larger than the values determined using XPS.

Effect of Catalyst Structure on CO Oxidation Activity.

Table 6.6 shows the specific turn over numbers (TON) and activation energies of CuCry catalysts for CO oxidation as a function of Cr/Al atomic ratio. The specific TON increases by a factor of 8 with increasing the Cr/Al atomic ratio from 0.0 to 0.054. However, further addition of Cr decreases the specific TON for CO oxidation. The

Cr/Al Atomic Ratio (x10 ²)	TON (s ⁻¹ x10 ²)	Activation Energy (kcal/mol)
0.0	4	17.9
1.3	15.3	16.5
2.7	24.3	14.4
5.4	31.5	15.8
8.0	16.2	16.2
10.7	19.7	17.5
13.4	15.2	16.3

Table 6.6. Turn Over Numbers^a and Activation Energies^b of CuCry Catalysts for CO Oxidation.

a- Determined from reaction rate at 240 °C normalized by Cu dispersion.

b- Estimated from Arrhenius plots within 15 % conversion.

activation energies of CuCry catalysts are independent of Cr content (16.4 \pm 1.1 kcal/mol). The CO oxidation activity can be attributed predominantly to the Cu species in CuCry catalysts, since Cr species show a little CO oxidation activity compared to Cu catalysts [6,13,19,23]. In this study, Cry catalysts showed negligible CO oxidation activity compared to CuCr0 catalyst at the same reaction condition. Addition of Cr up to a Cr/Al atomic ratio of 0.027 increases the TON by a factor of 6 compared to the CuCr0 catalyst. We attributed this to the formation of an active CuO phase which was observed in XRD patterns for CuCr1.3 and CuCr2.7 catalysts. In our previous work [51], we concluded that crystalline CuO was more active for CO oxidation reaction than Cu surface phase. This has been attributed to that redox ability of CuO/Al₂O₃ was more favorable than dispersed Cu surface phase during CO oxidation reaction [12].

It should be noted that CuCr5.4 catalyst shows the highest specific TON among the CuCry catalysts, although Cu and Cr dispersion decreases continuously as a function of Cr content. This has been correlated with the formation of CuCr₂O₄ phase on the CuCr5.4 catalyst which was detected by XRD. This is consistent with that satellite/main peak ratio of CuCr5.4 catalyst increases to 0.62 which is close to the value of pure CuCr₂O₄ (0.70) (Table 1). Therefore we attributed the activity improvement of CuCr5.4 catalyst to the formation of active phase (CuCr₂O₄). CuCr₂O₄ has been known more active catalyst than CuO for CO oxidation [4,13,19]. Severino and Laine [13] have studied alumina supported and unsupported Cu-Cr catalysts for CO oxidation. They suggested that chromium might enhance the catalytic activity by providing structure oxygen (O²) to copper species and electron transfer from copper to chromium. Kapteijn et al. [19] have also proposed recently that the Cu-Cr oxide catalyst was more active than a single oxide for CO oxidation due to more available of surface oxygen on the mixed oxide catalyst.

The further addition of Cr (Cr/Al atomic ratio ≥ 0.080) decreases CO oxidation activity for CuCry catalysts. XPS and XRD data indicate that the dispersions of both Cu and Cr are decreased significantly and a large CuCr₂O₄ crystalline phase is formed on the catalyst. In addition, excess Cr₂O₃ phase, which is not active for CO oxidation reaction, is present on the catalyst surface. Thus, low dispersion and covering active sites by excess Cr phase may decrease catalytic activity for high Cr content CuCry catalysts.

6.5. Conclusions

The combined use of several techniques to investigate the effect of Cr addition on the structure and CO oxidation activity of Cu/Cr/Al₂O₃ catalysts leads to the following conclusions.

1. Cu addition decreased Cr dispersion in CuCry catalysts (Cr/Al ≥ 0.054) compared to the Cr dispersion in analogue Cry catalysts. The dispersion of Cu species in CuCry catalysts also decreased with increasing Cr content. The decrease in dispersion of both Cu and Cr species has been attributed to the formation of large crystalline CuO, CuCr₂O₄, and Cr₂O₃ on the alumina support.

2. For CuCry catalysts with low Cr contents (Cr/Al \leq 0.027), the presence of highly dispersed Cr⁶⁺ phase inhibited the formation of copper surface phase and enhanced the formation of crystalline CuO over the alumina support. The CO oxidation activity increased in these catalysts (CuCr1.3 and CuCr2.7) has been attributed to an increase in the amount of crystalline CuO.

3. The CuCr5.4 catalyst showed the highest CO oxidation activity in this study. This is due to the formation of active $CuCr_2O_4$ phase. Post loaded copper species interacted with well dispersed Cr^{3^+} species to form $CuCr_2O_4$ rather than with highly dispersed Cr^{6^+} species or large Cr_2O_3 crystallites.

4. The CuCry catalysts with high Cr contents (Cr/Al ≥ 0.08) showed the decreased CO oxidation activity. This has been attributed to a decrease in the dispersion of Cu and Cr species and encapsulation of the active site with excess Cr₂O₃.

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6.6. References

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Chapter 7

The Influence of Surface Structure on the Catalytic Activity of Cerium Promoted Copper Oxide Catalysts on Alumina: Oxidation of Carbon Monoxide and Methane

7.1. Abstract

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been used to characterize a series of Cu/Ce/Al₂O₃ catalysts. Catalysts were prepared by incipient wetness impregnation using metal nitrates and alkoxides precursors. Catalyst loadings were held constant at 12 wt.% CuO and 5.1 wt.% CeO₂. Mixed oxide catalysts were prepared by impregnation of cerium first, followed by copper. The information obtained from surface and bulk characterization has been correlated with CO and CH₄ oxidation activity of the catalysts. Cu/Al₂O₃ catalysts prepared using Cu(II) nitrate (CuN) and Cu(II) ethoxide (CuA) precursors consist of a mixture of copper surface phase and crystalline CuO. The CuA catalyst shows higher dispersion, less crystalline CuO phase, and lower oxidation activity for CO and CH₄ than the CuN catalyst. For Cu/Ce/Al₂O₃ catalysts, Ce has little effect on the dispersion and crystallinity of the copper species. However, Cu impregnation decreases the Ce dispersion and increases the amount of crystalline CeO₂ present in the catalysts, particularly in catalysts prepared using the CeA support. Cerium addition dramatically increases the CO oxidation activity, however, it has little effect on CH_4 oxidation.

7.2. Introduction

Copper oxide is a well known component of catalysts for CO [1-6], hydrocarbon [1-3,7], chlorinated hydrocarbon [8] and alcohol oxidation [9,10] as well as for NO_x [11-13] and SO₂ reduction [13]. These air purification reactions using heterogeneous catalysts have been important topics due to their application to automobile exhaust converters and industrial waste incinerators. Copper oxide based catalysts have been considered as suitable substitutes for noble metal catalysts in emission control applications due to their high catalytic activity for the purification reactions, tolerant to SO₂ [3] and refractory to high temperature [14]. Several researchers reported that copper oxide based catalysts show similar activity to noble metal catalysts for CO oxidation [2], butanal and mercaptan oxidation [15], and reduction of NO by CO [13].

Rare earth oxide additives have been widely applied as textural and structural promoters for supported noble metal catalysts. Cerium addition prevents γ -alumina from sintering at high temperature and improves the dispersion and thermal stability of noble metals [16-20]. In addition, cerium oxide has been added to noble metal catalysts for treatment of automobile exhaust to promote the water-gas shift reaction [21,22], to suppress the CO inhibition effect [23-25], and to remove CO, hydrocarbons, and NO_x simultaneously using its oxygen storage ability [17,18,26-29].

Previous studies of rare earth promoters have focused primarily on their effects on the structure and activity of noble metal-based catalysts. The study of the promoters effect on supported transition metal oxide catalysts has been relatively limited. Recently cerium oxide has been studied both as a promoter [30] and as a support [31] for oxidation reactions over copper oxide based catalysts. Agarwal et al. [30] found that a ceria promoted hopcalite catalyst has a higher initial activity for hydrocarbon oxidation than a Pt catalyst. Bedford and LaBarge [31] showed that copper-chromium oxide impregnated on high surface area ceria has three-way catalyst behavior and retains catalyst activity after aging at high temperature. Flytzani-Stephanopoulos and coworkers [32-34] reported recently that a Cu-Ce-O composite catalyst shows high activity for CO and CH₄ oxidation and high resistance to water poisoning. They attributed the enhanced catalytic activity and stability to the strong interaction of copper and cerium oxides. The effect of a CeO_2 promoter on alumina supported copper oxide catalysts has been reported similar to the effect it has on noble metal catalysts [35,36]. The authors reported that the addition of CeO₂ enhances redox behavior of copper ion, increases dispersion of copper oxides, provides surface oxygen, and improves oxygen storage capacity of catalyst.

While, cerium oxide promoted copper oxide based catalysts have recently drawn an attention of many researchers, the effect of cerium oxide on the surface structure and reactivity of copper catalysts has not been studied extensively. The present work is part of a broad study to investigate structure-reactivity correlation for rare earth oxide promoted transition metal oxide based emission control catalysts. In this paper, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) have been used to determine the effect of catalyst precursors and cerium promotion on the chemical state and dispersion of copper oxide phases in a series of $Cu/Ce/Al_2O_3$ catalysts. The information derived from these techniques is correlated with CO and CH₄ oxidation activity to develop a more complete understanding of $Cu/Ce/Al_2O_3$ catalysts.

7.3. Experimental

Catalyst Preparation. Catalysts were prepared by pore volume impregnation of γ alumina (Cyanamid, surface area = 203 m²/g, pore volume = 0.6 mL/g). The alumina was finely ground (< 230 mesh) and calcined in air at 500 °C for 24 h prior to impregnation. The Ce/Al₂O₃ catalysts were prepared using a deionized water solution of ammonium cerium(IV) nitrate (Mallinckrodt Inc., Analytical Reagent) or an ethanol solution of cerium(IV) methoxyethoxide (Gelest Inc., 18-20% cerium methoxyethoxide in methoxyethanol). The impregnated sample derived from the aqueous cerium nitrate solution (designated "CeN") was dried in air at 120 °C for 24 h and calcined in air at 500 °C for 16 h. The sample prepared using the ethanol cerium methoxyethoxide solution (designated "CeA") was impregnated and subsequently dried at room temperature for 48 h in a N₂ purged glove bag prior to further drying in air at 120 °C for 24 h and calcination in air at 500 °C for 16 h. The Ce loading was held constant at 5.1 wt.% CeO₂. The Cu/Al₂O₃ catalysts were prepared with a deionized water solution of copper(II) nitrate (Columbus Chemical Industries Inc, ACS Grade) or an aqueous diethylenetriamine solution (DETA/water ratio = 1/3 by volume) of copper(II) ethoxide. DETA was

necessary due to the limited solubility of copper(II) ethoxide in water and common organic solvents. Since an aqueous DETA solution was used to dissolve copper(II) ethoxide, a Cu-DETA complex should be formed in the impregnating solution [37]. The impregnated samples derived from the aqueous copper nitrate solution (designated "CuN") and catalysts prepared with the aqueous DETA copper ethoxide solution (designated "CuA") were dried and calcined under the same conditions as used for CeN and CeA samples respectively. The Cu loading was held constant at 12 wt.% CuO. Mixed metal oxide catalysts were prepared by step-wise impregnation of Ce first, followed by Cu. The cerium modified alumina carrier was dried and calcined prior to introduction of copper. After the addition of copper, the catalysts were dried and calcined again at the same conditions described above depending on the choice of precursors. Catalysts prepared using nitrate and alkoxide precursors will be symbolized using "N" and "A", respectively.

Standard Materials. CuO and CeO₂ were prepared by calcining copper(II) nitrate and ammonium cerium(IV) nitrate in air at 500 °C for 16 h. CuAl₂O₄ was prepared by calcining stoichiometric amounts of the respective nitrates in air at 1000 °C for 24 h. CeAlO₃ was prepared by reduction of a dried CeA sample at 800 °C in H₂ (AGA, 99.99%) for 8 h. XRD patterns of the standard compounds matched the appropriate Powder Diffraction File [38].

BET Surface Area. Surface area measurements were performed using a QuantaChrome Quantasorb Jr. Sorption System. Approximately 0.1 g of catalyst were outgassed in a N₂/He mixture (5% N₂) at 350 $^{\circ}$ C for 1 h prior to adsorption

measurements. The measurements were made using relative pressures of N_2 to He of 0.05, 0.08, and 0.15 (N_2 surface area = 0.162 nm²) at 77 K. The addition of copper and/or cerium to the alumina carrier decreased the BET surface area by a maximum of 20 %.

X-Ray Diffraction. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer employing Cu K_{α} radiation ($\lambda = 1.5418$ Å). The X-ray was operated at 45 kV and 100 mA. Diffraction patterns were obtained using a scanning rate of 0.5 deg/min (in 2 θ) with divergence slit and scatter slit widths of 1°. Samples were run as powders packed into a glass sample holder having a 20 x 16 x 0.5-mm cavity.

The mean crystallite sizes (\overline{d}) of the CuO and CeO₂ particles were determined from XRD line broadening measurements using the Scherrer equation [39]:

$$\overline{d} = K\lambda / \beta \cos\theta \tag{1}$$

where λ is the X-ray wavelength, K is the particle shape factor, taken as 0.9, and β is the full width at half maximum (fwhm), in radians, of the CuO <111> or CeO₂<111> line.

Quantitative X-ray diffraction data were obtained by comparing $CuO<\overline{111}/Al_2O_3<400>$ or CeO_2 <111>/Al_2O_3<440> intensity ratios measured for catalyst samples with intensity ratios measured for physical mixtures of pure CuO or CeO₂ and γ -Al₂O₃. This method assumed that copper or cerium addition did not disrupt the γ -

 Al_2O_3 spinel and subsequently affect the intensity of the Al_2O_3 lines. The error in this method was estimated to be ± 20 %.

XPS Analysis. XPS data were obtained using a Perkin-Elmer Surface Science instrument equipped with a magnesium anode (1253.6 eV) operated at 300 W (15 kV, 20 mA) and a 10-360 hemispherical analyzer operated with a pass energy of 50 eV. The instrument typically operates at pressures near 1 x 10^{-8} torr in the analysis chamber. Spectra were collected using a PC137 board interfaced to a Zeos 386SX computer. Samples were analyzed as powders dusted onto double-sided sticky tape or spray coated onto a quartz slide using a methanol suspension of the catalyst. Binding energies for the catalyst samples and standard compounds which contained Al were referenced to the Al 2p peak (74.5 eV). The binding energies for standard compounds that did not contain Al were referenced to the C 1s line (284.6 eV) of the carbon overlayer. XPS binding energies were measured with a precision of ± 0.2 eV, or better.

Reduction of copper [40-42] and cerium [43-46] species during XPS experiments has been reported and attributed to several factors such as X-ray flux, X-ray dose, temperature, and pressure. In order to minimize the effect of photoreduction on the results, all samples were analyzed using the same distance between X-ray source and sample (\sim 3/4 inch) and minimum data acquisition time (5 min. scan for Cu 2p_{3/2} spectra). No significant photoreduction of copper species was observed using these experimental conditions. However, Ce 3d region had to be scanned for extended time (\sim 600 min.) in order to obtain reasonable quality spectra. Therefore Ce XPS data were used only for quantitative analysis to measure Ce dispersion on alumina. Quantitative XPS Analysis. It has been shown by Defosse et al. [47] that one may calculate the theoretical intensity ratio $I^{\circ}_{p}/I^{\circ}_{s}$ expected for a supported phase (p) atomically dispersed on a carrier (s). An extension of the Defosse model proposed by Kerkhof and Moulijn [48] has been used in the present investigation. The photoelectron cross sections and the mean escape depths of the photoelectrons used in these calculation were taken from Scofield [49] and Penn [50], respectively. For a phase (p) present as discrete particles, the experimental intensity ratio I_p/I_s is given by the following expression:

$$I_{p}/I_{s} = I_{p}^{\circ}/I_{s}^{\circ} \left[1 - \exp\left(-d/\lambda_{p}\right)\right] / d/\lambda_{p}$$
(2)

where I^{o}_{p}/I^{o}_{s} is the theoretical monolayer intensity ratio, d is the length of the edge of the cubic crystallites of the deposited phase and λ_{p} is the mean escape depth of the photoelectrons in the deposited phase.

CO Oxidation Activity. Measurement of CO oxidation activity was performed in a flow microreactor. Approximately 0.03 g of catalyst were supported on a glass frit (70 -100 μ m) and the temperature was measured with a K-type thermocouple located just above the catalyst bed. The reactor was heated by a tube furnace (Lindberg) with temperature being controlled within 1°C by an Omega CN 1200 temperature controller. Reactant gas flow rates were held constant with Brooks 5850 mass flow controllers. Product gases were analyzed with a Varian 920 gas chromatograph equipped with a TCD and interfaced to a Hewlett-Packard 3394A integrator. Reaction products were separated on a 6 ft 60/80 mesh Carbosieve S-II column. Prior to the first activity measurement, the catalyst was pretreated with a mixture of 5% O₂/He (99.5 % purity for O₂, 99.995% purity for He, AGA Gas Co.) stream (143 cc/min.) at 350 °C for 1 hr to remove any impurities absorbed on the surface during catalyst preparation and storage. CO oxidation reactions were performed with a constant flow rate (80 cm³/min) of 4.8% CO/9.8% O₂/85.4% He gas mixture (AGA, purity > 99.99%) in the temperature range of 100-220 °C. All activity measurements were obtained under steady-state conditions at conversions less than 15%.

CH₄ Oxidation Activity. Methane oxidation reactions were performed with a constant flow (15 cm³/min) of 0.98% CH₄/5.25% O₂/93.77% He gas mixture (AGA, purity > 99.99%) in the temperature range of 360-420 °C. Approximately 0.1 g catalyst were charged into the same type of microreactor used for CO oxidation measurements. Water produced during methane oxidation was frozen downstream from the reactor in a trap maintained < -40 °C with a mixture of ethanol and dry ice. No partial oxidation product was observed. All activity measurements were obtained under steady-state conditions at conversions less than 15%.

7.4. **Results and Discussions**

Chemical State and Dispersion of Cerium/Alumina Catalysts. The cerium oxide chemical state and dispersion of CeN and CeA catalysts have been reported previously [46]. In summary, the Ce dispersion for the CeN and CeA was found to be poor and similar each other (Table 7.2). For the CeA, only 0.3 wt.% cerium oxide was detectable

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by XRD (Figure 7.1b), indicating that most of the cerium oxide is present as an amorphous phase. A large amount of crystalline CeO₂ was observed for CeN (Figure 7.1c), although a low loading ceria and high surface area alumina were used in this study. This result does not agree with the results of other researchers [20,51]. For cerium catalysts with $< 2.6 \mu$ mol ceria/m² alumina, which is corresponding to $< 9 \text{ wt.}\% \text{ CeO}_2/200 \text{ m}^2 \text{ Al}_2\text{O}_3$, Ce species were present as CeAlO₃ dispersed surface phase and/or as small CeO₂ crystallites which were not detectable by XRD. This discrepancy may be readily understood when one considers that the cerium precursor used in this study (Ce⁴⁺) was different from the one used in other studies (Ce³⁺). The limited interaction between the Ce⁴⁺ precursor and alumina support may produce less Ce³⁺ ion occupancy in cation vacancies in alumina lattice due to charge conflict. This leads to the formation of CeO₂ during sample preparation.

Chemical State of Copper/Alumina Catalysts. The XRD patterns obtained for CuA and CuN catalysts are shown in Figure 7.1d and 7.1e. The XRD pattern of the CuN catalyst shows intense peaks characteristic of CuO, however, weak CuO lines are observed in the diffraction pattern of the CuA catalyst. Quantitative XRD measurements indicate that the CuN catalyst contains 5.5 wt.% crystalline CuO phase, while the CuA catalyst contains only 0.8 wt.% crystalline CuO (Table 7.1). For alumina supports with surface area comparable to that used in this study, previous results [40,52] suggest that up to 8 wt.% Cu can be incorporated into the alumina lattice as a Cu-Al₂O₃ surface phase when copper nitrate precursor is used to prepare the catalyst. Thus, our finding that the



Figure 7.1. XRD patterns measured for (a) alumina support, (b) CeA, (c) CeN, (d) CuA, and (e) CuN catalysts.
	Crystalline Phase (wt.%)		
Catalysts	CeO ₂	CuO	
CeN	4.6	b	
CeA	0.3	b	
CuN	b	5.5	
CuA	b	0.8	
CuNCeN	4.7	6.0	
CuACeN	4.1	0.6	
CuNCeA	3.4	5.5	
CuACeA	1.5	0.8	

Table 7.1.Concentration of Crystalline^a Phases in Cu/Ce/Al₂O₃Catalysts Calculated from Quantitative XRD Data.

a - Valid for crystalline phases with particle sizes > 3.0 nm.

b - Catalysts do not contain the component.

presence of 6.5 wt.% of CuO as a dispersed phase for CuN catalyst is in good agreement with previous work. In addition, the XPS Cu $2p_{3/2}$ binding energies measured for CuN and CuA catalysts (935.1 eV) are consistent with the value measured for CuAl₂O₄ (935.0 eV) and higher than the value measured for CuO (933.9 eV). Thus, the XRD and XPS results indicate that copper is present predominantly as a dispersed copper surface phase on the alumina support.

Dispersion of Copper Alumina Catalysts. Particle sizes determined from XRD line broadening calculations and from Cu/Al XPS intensity ratios for CuN and CuA catalysts are shown in Table 7.2. CuO particle sizes determined using XRD line broadening calculations are identical for CuN and CuA catalysts. While, the copper species particle size determined for the CuA catalyst using XPS is smaller than the value

	Particle Size (nm)				
Catalysts	Cerium		Copper		
	XRD	XPS	XRD	XPS	
CeN	5.1	1.6	- ²	_*	
CeA	4.5	1.6	_*	-*	
CuN	_ ^a	_ ^a	30	1.9	
CuA	- ^a	_ ^a	30	1.1	
CuNCeN	5.1	3.0	32	2.1	
CuACeN	5.4	3.6	32	1.1	
CuNCeA	4.1	4.1	32	2.2	
CuACeA	4.6	4.7	30	1.1	

Table 7.2.Particle Size of Cerium and Copper PhasesDetermined from XRD Line Broadening
Calculations and XPS Intensity Ratios.

a - Catalysts do not contain the component.

obtained for the CuN catalyst. XPS and XRD analyses of the CuA catalyst indicate the formation of less crystalline and more dispersed copper species on the alumina support compared to CuN catalyst. From quantitative XRD data, approximately 11.2 wt.% CuO in CuA which is not detected by XRD can be assigned as a dispersed copper species on the alumina surface. However, the relatively poor Cu dispersion compared to monolayer noted for CuA catalyst indicates that it is not entirely due to a Cu-Al₂O₃ surface phase, since copper surface phase is normally considered to be highly dispersed. It can be assumed that a poorly dispersed amorphous copper oxide phase is partially formed on CuA catalyst, which is not detectable by XRD. Uchikawa and Mackenzie [37] have proposed that a polymer structure of gel containing Cu-DETA unit was obtained after a

solution of copper ethoxide-aqueous DETA was heated at 90 °C. Therefore, the polymer structure is possibly obtained during the drying of aqueous copper ethoxide-DETA solution and then an amorphous CuO phase may be formed subsequently in calcination step. It is also possible that Cu-DETA complexes aggregate less during catalyst preparation than the copper nitrate precursor.

The CuO particle sizes of all copper catalysts determined with XRD are significantly larger than the values obtained from XPS (Table 7.2). This difference may be attributed to the limitations of X-ray diffraction. It is well known that XRD determined particle sizes are skewed to large values since XRD does not detect highly dispersed species. For the copper catalysts, a significant fraction of the Cu is present as a copper surface phase or small CuO particles (d < 3.0 nm) that are detected by XPS but not by XRD. Thus, smaller average particle sizes are expected from XPS calculations.

Chemical State of Copper/Cerium/Alumina Catalysts. Figure 7.2 shows the XRD patterns obtained for Cu/Ce/Al₂O₃ catalysts. The XRD patterns show only peaks characteristic of CuO and CeO₂. This is in agreement with studies have found that copper oxide is immiscible with cerium oxide [33]. For the Cu/Ce/Al₂O₃ catalysts prepared using the CeN (i.e. CuNCeN and CuACeN), Cu addition has little effect on the intensity of CeO₂ XRD peaks. This can be attributed to that a large amount of poorly dispersed crystalline CeO₂ (4.1 - 4.7 wt.%) is already present in CeN. For the Cu/Ce/Al₂O₃ catalysts derived from the CeA (i.e. CuNCeA or CuACeA), Cu addition increases the intensity of CeO₂ XRD peaks. The Cu addition effect on the CeO₂ peak intensity is observed more

Figure



Figure 7.2. XRD patterns measured for (a) CuACeA, (b) CuNCeA, (c) CuACeN, and (d) CuNCeN catalysts.

strongly in the diffraction pattern of CuNCeA catalyst than that of CuACeA catalyst. Quantitative XRD measurements (Table 7.1) show that Cu addition increases the amount of crystalline CeO₂ from 0.3 wt.% (CeA) to 1.5 wt.% (CuACeA) and 3.4 wt.% (CuNCeA). Since cerium oxide in CeA initially was a amorphous phase [46], post loaded copper species may act as a seed to form a crystalline CeO₂ during sample preparation. We attribute the more pronounced increase in crystalline CeO₂ content observed for the CuNCeA catalyst to the dissolution of cerium oxide in an acidic copper nitrate solution (pH 2.2) followed by agglomeration during subsequent drying and calcination steps of the catalyst preparation. Cerium oxide is insoluble in basic impregnating solution (pH 12.4) used for CuA derived catalysts.

For the Cu/Ce/Al₂O₃ catalysts, quantitative XRD measurements show that the CuO crystallinity is identical within experimental error to the value measured for analogous CuN and CuA catalysts. In addition, Ce has little effect on the XPS Cu $2p_{3/2}$ binding energies (935.0 ± 0.1 eV) which were identical to the value measured for CuAl₂O₄ and higher than the value of CuO. This indicates that chemical state of copper species is independent of Ce promoter in this study.

Dispersion of Copper/Cerium/Alumina Catalysts. The particle sizes of Cu and Ce species calculated using XRD line broadening and XPS intensity ratios are shown in Table 7.2. XRD line broadening calculations show that CeO₂ particle sizes of Cu/Ce/Al₂O₃ catalysts are not changed by Cu addition and are similar to those of analogous CeN and CeA supports. However, the cerium particle size calculated from Ce/Al XPS intensity ratios increases significantly after Cu addition. This indicates that the addition of copper species dramatically decreases the dispersion of cerium species. Since the addition of Cu increases the crystallinity of cerium oxide, we can attribute the decrease of dispersion to the agglomeration of cerium species during catalyst preparation step. In addition, we can not exclude an encapsulation phenomena involving the deposition of copper species on the surface of the cerium oxide phase, which would lead to a decrease in the Ce/Al XPS intensity ratio and dispersion subsequently. Such encapsulation effect would be more prominent for CuA due to its higher dispersion than CuN.

The particle sizes of copper oxide calculated from XRD line broadening calculations are identical regardless of cerium promotion and copper precursors. The particle sizes of copper species calculated from Cu/Al XPS intensity ratio depend only on the precursors used for catalyst preparation. The absence of a significant effect of Ce addition on the CuO crystallinity and dispersion can be understood in terms of the Ce/Al₂O₃ surface structure. Since the CeN and CeA contain a low concentration of poorly dispersed cerium oxide, most of the γ -Al₂O₃ surface is exposed to the Cu introduction. This exposed alumina dominates the alteration of the copper structure in the catalysts.

Effect of Catalyst Structure on CO Oxidation Activity. Table 7.3 shows the specific turnover numbers (TON) and activation energies for CO oxidation over Cu/Al_2O_3 and $Cu/Ce/Al_2O_3$ catalysts calculated at 160 °C using XPS estimates of the Cu dispersion. The results of CeN and CeA catalysts were not shown here due to their negligible CO oxidation activity compared to the copper catalysts. The CuN catalyst shows higher TON and lower activation energy than the values of the CuA catalyst. Comparison of the CO

	CO Oxidation		CH ₄ Oxidation	
Catalysts	TON	Activation Energy	TON	Activation Energy
CuN	1.1	12.0	3.7	22.7
CuA	0.3	15.4	1.2	21.6
CuNCeN	8.7	10.9	3.7	22.7
CuACeN	3.0	12.1	1.3	23.8
CuNCeA	13.7	12.6	4.5	21.9
CuACeA	1.5	12.8	1.4	22.6

Table 7.3.Turn Over Numbers* and Activation Energies* of
Cu/Ce/Al2O3 Catalysts for CO and CH4 Oxidation.

a - Calculated at 160 °C and 390 °C for CO and CH₄ oxidation respectively using exposed Cu species determined from XPS (s⁻¹ x 10²).

b - Estmiated from Arrhenius Plots (kcal/mol) within 15 % conversion.

oxidation activities measured for the CuN and CuA catalysts indicates that the catalyst containing more crystalline CuO (i.e. CuN) is more active than catalysts containing less CuO phase (CuA). This is consistent with our previous study [53], which showed that crystalline CuO was more active for CO oxidation than a dispersed copper surface phase.

The Ce promoted catalysts show increased TONs by a factor of 5 to 12 compared to unpromoted copper catalysts. The activation energies for CO oxidation calculated for cerium promoted catalysts are similar within a experimental error $(12.1 \pm 0.9 \text{ kcal/mol})$. The higher CO oxidation TON for cerium promoted copper catalysts indicates that cerium oxide is very effective promoter when one considers that only a small amount of cerium oxide (5.1 wt.%) was used in this study. Changing crystallinity and dispersion of cerium oxide species after Cu addition indicates that copper oxide interacts strongly with cerium oxide during catalyst preparation. Therefore, cerium species included in the CuO particles

may lead to increased CO oxidation activity. Liu and Flytzani-Stephanopoulos [33,34] reported that Cu-Ce-O composite catalyst shows high CO oxidation activity, comparable to that of the Pt/alumina catalyst. They attributed the enhanced catalytic activity to the strong interaction of copper and cerium oxides. It also has been reported recently [35,36] that ceria promoter enhances the redox behavior of copper ions and produces surface oxygen ions over CuO/CeO₂/ γ -alumina catalysts. The Cu/Ce/Al₂O₃ catalysts derived from CuN show higher CO oxidation activity than the catalyst prepared with CuA. This is consistent with the result of CuN and CuA catalysts, which shows higher CO oxidation activity for the catalyst containing more crystalline CuO.

Effect of Catalyst Structure on CH₄ Oxidation Activity. Table 7.3 shows the specific turnover numbers (TON) and activation energies for CH₄ oxidation calculated at 390 °C. The results of CeN and CeA catalysts were not shown here due to their negligible CH₄ oxidation activity compared to the copper catalysts. The TONs of the catalysts derived from CuN is about 3 times higher than the catalysts prepared with CuA. The Ce addition has little effect on the CH₄ oxidation TON for copper catalysts. The activation energies are identical within experimental error (22.6 \pm 0.8 kcal/mol).

Since the active site of copper oxide catalyst for CH₄ oxidation reaction has been assigned to the isolated copper surface phase [53], the catalyst containing more isolated copper surface phase should be more effective. In our study, CuA catalyst may contain less isolated copper surface phase than CuN catalyst, although Cu dispersion of CuA is higher than that of CuN. The formation of less isolated copper surface phase can be attributed to the formation of Cu-DETA polymer structure during catalyst preparation step [37]. We propose that this polymer type Cu-DETA complex leads to the formation of an interacting copper surface phase (i.e. clustered copper species) and/or amorphous copper oxide which may be a less active phase than isolated copper species for CH_4 oxidation. The no cerium promoter effect on CH_4 oxidation reaction for $Cu/Ce/Al_2O_3$ catalysts can be explained by little interaction between poorly dispersed cerium oxide and isolated copper surface phase.

7.5. Conclusions

The combined use of several techniques to investigate the effect of cerium promoter and metal precursors on the structure of Cu/Ce/Al₂O₃ catalysts leads to the following conclusions.

1. The CuA catalyst shows enhanced Cu dispersion compared to CuN catalyst. However, CuA catalyst is less active for CO and CH₄ oxidation than CuN catalyst. This has been attributed to that CuA catalyst contain less active phases than the CuN catalyst for CO and CH₄ oxidation which are crystalline CuO and isolated copper surface species, respectively.

2. Ce has little effect on the dispersion and crystallinity of copper species. Whereas Cu addition decreases the Ce dispersion and increases the amount of crystalline CeO₂ present in the Cu/Ce/Al₂O₃ catalysts particularly in catalysts prepared using the CeA. 3. Ce addition increases the CO oxidation activity of the copper catalysts. This has been attributed to that cerium oxide interacts strongly with CuO crystalline which is active phase for CO oxidation. While, the Ce may not promote the isolated copper surface species which is active site for CH_4 oxidation.

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7.6. References

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